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SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.–Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Meteorology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. – Publisher.

POSSIBLE CAUSES OF THE VERTICAL HYDROCHEMICAL ZONALITY OF ARTESIAN WATER

O. Ya. Samoilov and D. S. Sokolov

The hydration of ions in aqueous solutions has been regarded [1,2] as the action of ions on the translational motion (activated jumps) of neighboring water molecules of the solution. In this paper we attempt to apply previous results to the solution of the problem of the vertical hydrochemical zonality of artesian water, which is itself part of the problem of the formation of subterranean waters. The most difficult and controversial problem is that of the causes of the phenomenon observed in the great majority of artesian basins, namely, regular change with depth from bicarbonate waters, to sulfate waters, and further to chloride waters, which increase in concentration until brines are found (general case of vertical zonality). It must be pointed out that in most cases the chemical composition of artesian water does not correspond with the composition of the rocks in which the water is found.

The difficulty of explaining the causes of vertical zonality will remain irrespective of whether the formation of brines is associated with the metamorphosis of waters of marine origin or whether the latter are considered to take no part at all. Correspondingly, as causes of this zonality different investigators have suggested various combinations of a great diversity of processes (redistribution of water-soluble salts between rocks and subterranean waters by dissolution and leaching, diffusional leaching, cation exchange, pressing-off of solutions in the lithification of precipitates, decomposition of water molecules under the influence of radioactive processes, subterranean evaporation, and others). In the evaluation of the parts played by these processes diametrically opposed views have been expressed [3, 4].

In this matter a special position is occupied by Filatov's hypothesis [5], which associates the vertical hydrochemical zonality of artesian water with gravitational phenomena. We must point out that the correspondence found by Filatov between the distribution of ions in various vertical zones and the values of what he called "ionic density" is associated with the use of old values of the ionic radii of HCO_3^- and SO_4^{2-}. From the physicochemical point of view Filatov's hypothesis has no foundation, but we must point out that it is essentially the first attempt to associate the characteristics of vertical hydrochemical zonality with phenomena occuring in the aqueous solutions themselves.

In the present paper the vertical hydrochemical zonality observed in most artesian basins is explained by processes occurring in solutions under conditions of extremely slow movement of subterranean water from upper horizons of the lithosphere into deep artesian strata, in which the hydrostatic pressure is high, and further to the discharge centers. These processes occur both when there is penetration of infiltrating water (the ionic composition of which is established primarily by leaching in the upper horizons of the earth's crust) into artesian horizons and also when a region passes from below sea level and for some time water of marine origin is preserved in the component rocks of the region but is gradually displaced by infiltering waters. Undoubtedly, whereas "normal" vertical zonality may attain a certain specificity and may be more or less clearly defined, depending on the structure of the given artesian basin, the peculiarities of its geological history, and the composition of the waters penetrating down from the upper horizons of the lithosphere, on the other hand the regularities are often absent, being obscured by the action of other factors, e.g., high rates of movement of subterranean waters, influx of carbonate waters, biochemical processes.

Let us consider how thermal, particularly translational (advancing, transference), motion of ions and water molecules of a solution proceeds under the conditions of slow downward movement of artesian water accompanied by gradual increase of pressure. Translational movement of ions and water molecules in solutions consists mainly in activated jumps from one equilibrium position of the solution structure to a neighboring one [6-8]. In this process some ions make activated jumps together with the nearest water molecules and others mainly without these accompanying molecules (i.e., move as individual ions). An equation has been given which determines relative parts played by different jumps in the translational motion of various ions [2]. According to this equation, the thermal motion of ions most extensively found in natural waters (excluding Mg^{2+}), consists mainly in jumps of individual ions, i.e., is associated with exchange of water molecules closest to the ions. With increase in pressure the activation energy of such jumps increases; in fact, increase in pressure can result only in strengthening of bonds between an ion and the nearest water molecules. Increase in pressure leads, therefore, to difficulty of exchange between these molecules. On the other hand, in pure water increase in pressure results in breakdown of the open tetrahedral structure: bonds between molecules are broken and activation energy for self-diffusion diminishes [9]. The well known "anomalous" viscosity of water is associated with this behavior.

Let the pressure at depth h be p, increasing to p + Δp at depth h + Δh. Then in accordance with the theory of activated jumps of particles of liquids (6, 10], the average number of jumps of particles (ions and water molecules) of a solution in the downward direction in unit time at depth h will be:

$$j_p = \frac{1}{6} j_0 e^{-(E+\Delta E)/RT}, \tag{1}$$

and at depth h + Δh it will be:

$$j_{p+\Delta p} = \frac{1}{6} j_0 e^{-(E+\Delta E+\gamma)/RT}, \tag{2}$$

in which j_0 is a coefficient (pre-exponential factor); the factor $\frac{1}{6}$ is associated with the fact that the number of jumps in a given direction is being considered; R is the gas constant; T is the absolute temperature; E + ΔE is the activation energy for the jump (self-diffusion); and $\gamma = \gamma(\Delta p)$ is the increment of activation energy of self-diffusion associated with increase in pressure. ΔE is the change brought about by ions in the potential barrier for activated jumps of water molecules close to ions, as compared with the potential barrier for pure water [1]. ΔE values characterize the hydration of ions in solutions. It was shown that for some ions ΔE is positive, and for others negative, i.e., there is negative hydration[1]. Subtracting (2) from (1) we have :

$$\Delta j = j_p - j_{p+\Delta p} = \frac{1}{6} j_0 (1 - e^{-\gamma/RT}) e^{-E/RT} \cdot e^{-\Delta E/RT},$$

or

$$\Delta j = A e^{-\Delta E/RT}, \tag{3}$$

in which

$$A = \frac{1}{6} j_0 (1 - e^{-\gamma/RT}) e^{-E/RT} *.$$

For water molecules not in the immediate surroundings of ions, Δj = A, since ΔE = 0. The sign of A is clearly determined by that of $1 - e^{-\gamma/RT}$, for the other factors are always positive. As pointed out above, with increase in pressure for individual ions the activation energy of jumps increases and for water molecules it diminishes.

* The component associated with the general movement of artesian water is not considered, since it is the supplementary streams that are being calculated.

Therefore, for ions $e^{-\gamma/RT} < 1$ and $A > 0$, and for water molecules $e^{-\gamma/RT} > 1$ and $A < 0$. Hence, in accordance with Equation 3, the increase of pressure with depth causes a supplementary stream of ions downward which is superimposed on the general movement of the artesian water to deeper horizons. For the water molecules, however, the supplementary stream is in the opposite direction (upward). It is probably with these movements that the generally observed increase in the mineralization of artesian water with depth is associated. *

The formation of concentration gradients inevitably results in diffusion currents of matter in the direction of equalization of concentrations. Under some conditions diffusion might suppress the process under consideration. However, diffusion (upward) is rendered difficult by the countercurrent of artesian water moving downward. The slower the down movement of water, the greater the effect of diffusion. It is understandable that small values of Δh correspond to very small values of Δp, but in accordance with the theory of activated jumps the streams of particles observed in liquid that is in an external field are due to very small, but directed perturbations in the Brownian jumping movements of the particles: The average number of activated jumps of particles (e.g., in 1 ml of liquid per second) is enormous, so that very small perturbations, if they have a directed character, cause macroscopic streams [7]. Moreover, it must not be forgotten that the observed increase in mineralization of artesian water with depth is the result of a process occurring for a long time in the geological sense.

In accordance with Equation (3), increase of pressure with depth is associated with the existence of a supplementary downward stream of all ions. However, for different ions the supplementary streams and supplementary velocities in the direction of increase of pressure are different. It is clear that the movements of the different ions will proceed under the conditions of maintenance of the electrical neutrality of the solution as a whole. The magnitudes of the streams are determined mainly by the values of the exponential factor of Equation (3). The stream is the larger, the lower ΔE. For ions having positive values of ΔE the stream is small, but it becomes larger as ΔE diminishes. The stream is larger at negative ΔE, i.e., in the case of negatively hydrated ions. As ΔE becomes more negative, the stream becomes substantially larger. **

In the case of ions with negative hydration, on the one hand the supplementary rates of the down movements of ions are relatively high, and on the other hand the variation in rates for different ions is great (for negative ΔE the variation in the values of the exponential factor of Equation (3) for differentions is comparatively great). Negative hydration is peculiar to most of the anions that are most widely found under natural conditions. Hence, in the case of anions the variation in values of ΔE results in the formation of clearly defined zones of vertical hydrochemical zonality. In the case of cations we may speak only of the tendency of ions with high positive values of ΔE to be concentrated in the upper water-bearing horizons of artesian basins.

The values of ΔE for anions are the lower, the lower the temperature coefficient α_i of the anion mobility. At 21.5° for the anions CO_3^{2-}, SO_4^{2-}, Cl^-, Br^-, and I^-, $100\alpha_i$ has the respective values 2.70, 2.37, 2.16, 2.15, and 2.13 [11, 12]. For HCO_3^- α_i has not been determined, but it may be asserted that $\Delta E_{HCO_3^-} > \Delta E_{SO_4^{2-}}$. In fact, the S–O distance in the SO_4^{2-} ion is 1.50 A [13, 14], and the C–O distance in the CO_3^{2-} ion is 1.31 A [15], so that the average C–O distance in the HCO_3^- ion (which is undoubtedly very close to the corresponding distance in the CO_3^{2-} ion) is less than the S–O distance in the SO_4^{2-} ion. Hence, the relative sizes of the HCO_3^- and SO_4^{2-} ions are such that movement of an SO_4^{2-} ion in a solution must be more restricted than that of an HCO_3^- ion. Moreover, $u_{HCO_3^-} < {}^1/_2\, u_{SO_4^{2-}}$ (u is ionic mobility). It must be concluded that the activation energy of exchange of the nearest water molecules is greater for the HCO_3^- ion than for the SO_4^{2-} ion, i.e., that $\Delta E_{HCO_3^-} > \Delta E_{SO_4^{2-}}$ (the HCO_3^- ion is hydrated more strongly than the SO_4^{2-} ion). $\Delta E_{HCO_3^-}$ is probably close to the comparatively high positive value of $\Delta E_{CO_3^{2-}}$, so that, in general, the HCO_3^- ion does not undergo negative hydration.

Thus, with respect to reduction in the value of ΔE, the anions occurring most extensively in natural waters form the following series:

$$HCO_3^- > SO_4^{2-} > Cl^- > Br^- > I^-.$$

* The change with depth of average number of activated jumps of particles of solutions is due to several factors (pressure, temperature, concentration of solutions, and others). The geothermal gradient acts in the same direction as increase in pressure: with rise in temperature the mobility of negatively hydrated ions (and therefore also the average number of activated jumps in unit time) rises less than the mobility of water molecules.

** At $\Delta E = 0$ the exponential factor of Equation (3) passes through unity and with further fall in ΔE it increases fairly sharply.

It will be obvious that for the supplementary rates of down movement of anions in artesian water we have the series:

$$HCO_3^- < SO_4^{2-} < Cl^- < Br^- < I^-.$$

It is with this that the observed phenomenon of vertical hydrochemical zonality of artesian water may be associated. Actually, the rate of movement of this water as a whole falls off with increased depth. Correspondingly, in the upper artesian horizons there is more intense discharge and there is an overflow of excess of solutions from the general stream of artesian water. It will be clear that these solutions will have a higher content of the anions having a relatively smaller supplementary downward stream. Hence, as the artesian water as a whole sinks, there is a gradual disappearance from its composition first of HCO_3^-, and then of SO_4^{2-}, which are extended in discharge and do not attain lower horizons. The slower the downward movement of a given ion, the less the depth at which it has almost disappeared from the artesian water. At deep artesian horizons the prevailing solutions are enriched in anions having the highest rates of downward movement (Cl^-, Br^-, I^-). * As there is a simultaneous increase in mineralization, the curves for the relation between HCO_3^- and SO_4^{2-} concentrations and depth must pass through maxima (see figure).

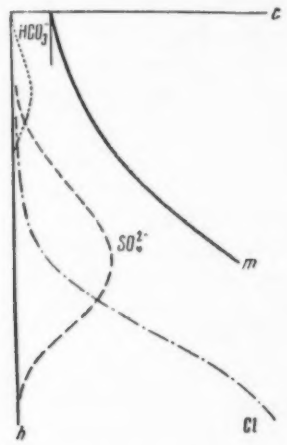

Diagram of variation of concentration (c) of anions in artesian water and of rise in mineralization (m) with depth (general case). The m curve is displaced along the axis of abscissae.

In accordance with the views that we have expressed above, the observed vertical hydrochemical zonality of artesian water is a consequence of a peculiar kind of barodiffusion occurring in the course of a geologically long time. In this an important part is played by ions that show negative hydration. It must be pointed out that it was not proposed to make any detailed examination of the problem of vertical zonality in the present paper. It was proposed only to draw attention to the possible connection between this phenomenon and the mechanism of self-diffusion and hydration of ions in aqueous solutions. However, it is in no way denied that under natural conditions this connection may be frequently obscured by the operation of other factors.

In conclusion we may point out that, in general, since the translational motion of ions and water molecules in solutions depends on ΔE values, to a large extent migration of various ions in aqueous solutions under geological conditions also depends on these values. ΔE values and, in particular, the phenomenon of negative hydration must therefore be of great significance in the geochemistry of several elements.

SUMMARY

1. The problem of the vertical hydrochemical zonality of artesian water must be regarded in its association with the hydration of ions in solutions and the peculiarities of the thermal motions of ions and water molecules in solutions.

2. Under the conditions of the slow downward movement of artesian water these peculiarities result in the formation of supplementary streams of particles which are superimposed on the general movement of the artesian water. It can be shown that with these supplementary streams there are associated both increase in mineralization of subterranean waters with increase in depth, and also a regular change from bicarbonate waters, to sulfate waters, and then to chloride waters.

* For K^+, $\Delta E < 0$ [2] and the content of K^+, like those of Cl^-, Br^-, and I^-, must rise appreciably in deep artesian horizons. However, in view of the very low concentration of K^+, as compared with those of Na^+, Ca^{2+}, and Mg^{2+}, in subterranean waters and in view of the inadequate number of relevant analyses, our knowledge of this matter is only very tentative. Cases are known, however, in which this view has been confirmed (see e.g., [4], p. 97).

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** Russian translation.

PROTECTIVE POTENTIALS OF METALS

V. V. Gerasimov

The electrochemical protection of metals finds ever-increasing application in various branches of the national economy. One of the main problems associated with electrochemical protection is the calculation of the protective potential. There have been several attempts at calculating the value of the protective potential [1-4], but not one of them can be regarded as satisfactory.

In the calculation of the protective potential of iron, Harrel and Clerc [1] assume quite arbitrarily that 1) the protective potential corresponds to that state of iron for which the sum of the concentrations of ferrous ions ($c_{Fe^{++}}$) and hydroxyl ions (c_{OH^-}) is a minimum, and 2) the relation between the potential of the iron and the concentration of its ions in solutions saturated with oxygen is expressed by the Nernst equation.

According to Harrel and Clerc, the determination of the protective potential consists in the simultaneous solution of two equations:

$$c_{Fe^{++}} \cdot c^2_{OH^-} = 1.65 \cdot 10^{-15}, \tag{1}$$

$$E^0_{Fe^{++}} + \frac{0.059}{2} \log c_{Fe^{++}} = E^0_{OH^-} - 0.059 \log c_{OH^-}. \tag{2}$$

in which $E^0_{F^{++}} = -0.44$ v, the normal electrode potential of iron, and $E^0_{OH^-} = -14 \cdot 0{,}059 = -0.829$ v.

Substituting numerical values in Equation (2) and making suitable transformations, we obtain

$$c_{Fe^{++}} \cdot c^2_{OH^-} = 63 \cdot 10^{-15}. \tag{3}$$

Graphical construction, which is carried out in Fig. 1, shows that Equations (1) and (2) are incompatible, so that calculations based on their simultaneous solutions [1, 2] are incorrect.

Zhuk [3] and various other authors assume that the equilibrium potential of the metal can be regarded as the protective potential irrespective of whether there are ions of the given metal in the solution, or there are other ions and molecules that may take part in electrode reactions. Let us consider the case in which the solution contains not only ions of the metal but also hydrogen ions and a saturation concentration of oxygen. We shall denote the rate of ionization of the metal by F_1 and the rate of the reverse reaction – transfer of ions from the solution – by F_2. We shall denote the rate of formation of hydrogen molecules from hydrogen ions by F_3 and the rate of the reverse reactions of ionization of hydrogen molecules by F_4. We shall further denote the rate of reduction of oxygen by F_5 and the rate of the reverse reaction by F_6. Under stationary conditions, from the constancy of the number of charges on the surface it follows that

$$F_1 + F_4 + F_6 = F_2 + F_3 + F_5. \tag{4}$$

The rate of solution of the metal is

$$F_1 - F_2 = F_3 + F_5 - F_4 - F_6. \tag{5}$$

If the potential established in the dissolution of the metal is considerably more negative than those of the reversible hydrogen and oxygen electrodes, F_4 and F_6 in Equations (4) and (5) may be neglected:

$$F_1 - F_2 = F_3 + F_5. \tag{6}$$

It follows from Equation (6) that the rate of solution (corrosion) of the metal will be determined in this case by the rate of hydrogen and oxygen depolarization. An analogous case for the dissolution of lead in acid was analyzed in detail by Kolotyrkin and Frumkin [5]. Our experiments show that copper in 0.1 M $CuSO_4$ and cadmium in 0.1 M $CdSO_4$ (solutions saturated with oxygen) corrode in spite of the fact that in each case the potential of the metal has almost the equilibrium value (Table 1).

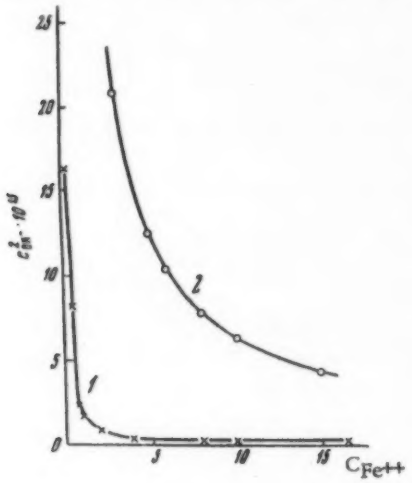

Fig. 1. Graphical representation of equations: 1) Equation (1); 2) Equation (2).

Let us examine the case in which ions of the given metal are absent. Let us place the metal (iron, say) in sodium chloride solution. From an outside source let us polarize the sample to a potential corresponding to the equilibrium potential of iron ($\varphi_{c^0_{Fe}}$), at a concentration of metal ions determined by the solubility product of the iron compound FeR:

$$[c^0_{Fe}]\,[c^0_R] = \text{const}. \tag{7}$$

As the concentration of ferrous ions, both in the solution and in the layer in contact with the electrode, is practically zero, the rate of transfer of ions from the solution F_2 will be less than the rate of solution of metal F_1. Owing to dissolution of metal, some ferrous ions will appear in the layer in contact with the electrode. If the solution is vigorously stirred and the rate of diffusion of ferrous ions from this surface layer F_3 is greater than F_1, the concentration of ferrous ions c^0_{Fe}, corresponding to the solubility product, will not be attained. Consequently, at a potential φc^0_{Fe}, F_2 will always be less than F_1 and the metal will corrode. In the solution in which the corrosion process occurs the concentration of foreign salts (e.g., sodium chloride) is generally higher than that of ferrous ions, so that the current will be mainly carried by sodium and chloride ions and the action of the electric field on the diffusing ferrous ions may be neglected.

TABLE 1

Reversible Potentials and the Corrosion of Metals in Solutions of their Own Ions

Metal	Medium	Reversible potential with respect to standard hydrogen electrode		Rate of corrosion $k \cdot 10^4$ (g/sq·dm·day)
		Calculated	Measured	
Copper	0.1 *M* $CuSO_4$	+0.293	+0.303	185
Cadmium	0.1 *M* $CdSO_4$	−0.453	−0.440	253

If $F_3 < F_1$, there is established in the electrode surface layer a concentration of ferrous ions c_{Fe} determined by the relation between F_1, F_2, and F_3.

At the given potential φ^0_{cFe}

$$F_1 = k_1 \exp \frac{\beta F}{RT} \varphi_{c^0_{Fe}}, \tag{8}$$

$$F_2 = k_2 c_{Fe} \exp - \frac{\alpha F}{RT} \varphi_{c^0_{Fe}}, \tag{9}$$

$$F_3 = k_3 D c_{Fe}, \tag{10}$$

in which k_1, k_2, and k_3 are constants, α, β, F, R, and T have their usual meanings, and D is the diffusion coefficient for ferrous ions. Under stationary conditions with constant concentration of ferrous ions in the surface layer:

$$F_1 = F_2 + F_3. \tag{11}$$

$$K_1 \exp \frac{\beta F}{RT} \varphi_{c^0_{Fe}} = \left(k_2 \exp \frac{-\alpha F}{RT} \varphi_{c^0_{Fe}} + k_3 D\right) c_{Fe}, \tag{12}$$

$$c_{Fe} = \frac{k_1 \exp \frac{\beta F}{RT} \varphi_{c^0_{Fe}}}{k_2 \exp \frac{-\alpha F}{RT} \varphi_{c^0_{Fe}} + k_3 D}. \tag{13}$$

As we chose φ^0_{cFe} as the equilibrium potential of iron for a concentration c^0_{Fe} of its ions, we have

$$k_1 \cdot \exp \frac{\beta F}{RT} \varphi_{c^0_{Fe}} = k_2 c^0_{Fe} \exp \frac{-\alpha F}{RT} \varphi_{c^0_{Fe}}, \tag{14}$$

$$c^0_{Fe} = \frac{k_1 \exp \frac{\beta F}{RT} \varphi_{c^0_{Fe}}}{k_2 \exp \frac{-\alpha F}{RT} \varphi_{c^0_{Fe}}}. \tag{15}$$

Comparison of Equations (13) and (15) shows that $c_{Fe} < c^0_{Fe}$, i.e., the concentration of ferrous ions that is established is less than c^0_{Fe}, which we assumed in selecting the protective potential φ^0_{cFe}. The potential φ^0_{cFe}, therefore, is not the equilibrium potential at the established concentration c_{Fe}, and the rate of solution of the metal $F_1 - F_2$ will be proportional to the rate of diffusion of metal ions from the surface layer.

It follows from this discussion that whatever concentration of ferrous ions in the surface layer we may aim at attaining and whatever value the calculation of the corresponding equilibrium potential may give, the concentration of ferrous ions that will be established will always be less than the equilibrium value, Equation (11) will hold at this potential, and the metal will corrode. Experimental verification showed that the equilibrium potential of iron calculated from the concentration of ferrous ions determined from the solubility product of $Fe(OH)_2$ (equal, according to Zhuk [3] to from -0.514 to -0.618 v with respect to the standard hydrogen electrode), is not the protective potential. Thus, the rate of corrosion of iron in 1.5% sodium chloride solution at a potential of -0.618 v is 0.0072 g/ sq. dm·day. It must not be forgotten that at the equilibrium potential

the rate of the anode reaction of dissolution of metal is not zero, but equal to the rate of the reverse reaction of discharge of metal ions.

The mechanical properties of metal deposited from solution as a result of the discharge of its ions are not identical with the properties of cast or rolled metal. On this basis, electrochemical protection should ensure not only constancy of weight of the metal, which is attained when $F_1 = F_2$, but also reduction in the rate of ionization of the metal F_1.

The invalidity of the above-considered methods of calculating protective potentials makes it necessary to find a rational method of calculating these values, and the next part of this paper is devoted to this matter. As our premises for the calculation of the protective potential we assume the following: if in the process of anodic dissolution of metal the slowest stage is ionization of the metal, the rate of the anode reaction of dissolution of metal (i_a), and consequently also rate of corrosion – is, in accordance with the principles of electrochemical kinetics, determined by the potential of the metal (other conditions being equal) in the following manner:

$$i_a = k \exp \frac{\varphi \beta n F}{RT}. \tag{16}$$

At the stationary potential of the metal that is established (φ_{st}), the rate of the anode process $i_{a_{st}}$ is

$$i_{a_{st}} = k \exp \frac{\varphi_{st} \beta n F}{RT}. \tag{17}$$

On attainment of the protective potential φ_p the rate of the anode process i_{a_p} is

$$i_{a_p} = k \exp \frac{\varphi_p \beta n F}{RT}. \tag{18}$$

Dividing Equation (17) by Equation (18) and carrying out simple transformations, we obtain

$$\varphi_p = \varphi_{st} - b \log \frac{i_{a_{st}}}{i_{a_p}}; \qquad b = \frac{RT}{\beta n F} 2.3. \tag{19}$$

The results of several authors [6-8], which are presented in Figures 2 and 3, show that there is a linear relationship between the logarithm of the rate of corrosion of the metal and its potential.

Most of the experimentally found values of "b" given in Table 2 are within the range 0.07-0.09 v, i.e., somewhat higher than the value of "b" calculated for $\beta = 1/2$ and $n = 2$. However, these values are close to the value of b obtained by Kolotyrkin and Frumkin [9] in the investigation of the relation of the potential of nickel in hydrochloric acid solution to the rate of anodic dissolution. In the calculation of protective potentials we may assume for practical purposes that b = 0.1 v. Hence, for the calculation of protective potential from Equation (19) it is essential to know 1) the stationary potential of the metal φ_{st}, and 2) the rate of corrosion at φ_{st} ($i_{a_{st}}$), and so find the rate of corrosion at φ_p (i_{ap}).

The rate of corrosion of steel at φ_p is selected on the basis of the permissible corrosion losses of the protected system. We carried out an experimental verification of Equation (19). For i_{ap} we assumed the value 10^{-4} g / sq. dm·day, the least corrosion losses that can be measured when weighing on an analytical balance weighing within 10^{-4} g. Since $i_{a_{st}}$ is expressed in the same units as i_{a_p}, Equation (19) acquires the simple form

$$\varphi_p = \varphi_{st} - 0.1 \log i_{a_{st}}. \tag{20}$$

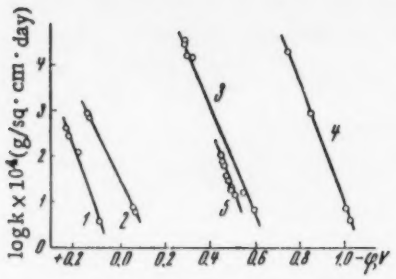

Fig. 2. Relation between the logarithm of the rate of corrosion and the potential of the metal: 1) copper in 0.1 N HNO_3; 2) copper in 0.1 n HCl; 3) iron in 0.1 n HCl; 4) zinc in 0.1 n HCl; 5) iron in 0.05% Na_2SO_4; 6) iron in 0.05% NaCl.

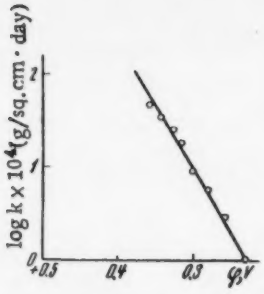

Fig. 3. Relation between the logarithm of the rate of corrosion of copper in 0.8 N CuCl and the potential (according to N. D. Tomashov).

TABLE 2

Experimentally Found Values of "b"

Metal	Medium	Value of "b" (v)	Literature reference
Copper	0.1 *N* HNO_3	0.070	[6]
Copper	0.1 *N* HCl	0.095	[6]
Iron	0.1 *N* HCl	0.084	[6]
Zinc	0.1 *N* HCl	0.075	[6]
Iron	0.05% Na_2SO_4	0.075	[8]
Iron	0.05% NaCl	0.072	[8]
Copper	0,8 *N* CuCl	0.070	[7]

From the experimentally determined values of $i_{a_{st}}$ and φ_{st} we calculated the protective potentials of copper, zinc, cadmium, magnesium, lead, iron, and cast iron in 1.5% sodium chloride solution and of iron in artificial lake water (0.012% NcCl). We determined the corrosion losses of these metals at the protective potentials calculated from Equation (20). The experimental data are given in Table 3, and they show that the rates of corrosion of these metals, with the exception of lead, at the protective potentials calculated from Equation (20) differ from the values of i_{a_p} assumed in the calculation by not more than $1 \cdot 10^{-4}$, i.e., there is quite satisfactory agreement between experimental and calculated values and Equation (19) can be used for the calculation of protective potentials.

TABLE 3

Calculated and Experimentally Determined Values of Protective Potentials for Metals in 1.5% Sodium Chloride Solution

Metal	φ_{st} w.r. to stand. H electrode (v)	$i_{a_{st}} \cdot 10^4$ (g/sq.dm·day)	$\log (i_{a_{st}} \cdot 10^4)$ g/sq.dm·day	φ_p w.r. to stand. H electrode (v)	Rate of corrosion at φ_p ($i_{a_p} \cdot 10^4$ in g/sq.dm·day)
Copper	+0.030	21	1.32	—0.102	0.0
Zinc	—0.800	370	2.57	—1.057	0.0
Cadmium	—0.500	246	2.39	—0.739	0.0
Magnesium	—1.300	1350	3.13	—1.613	0.0
Lead	—0.310	125	2.1	—0.520	5.0
Iron	—0.503	118	2.07	—0.710	1.0
Cast iron	—0.460	182	2.6	—0.720	0.5
Iron in artificial lake water	—0.442	104	2.02	—0.644	2.0

The proposed method of calculating protective potentials cannot be used when 1) passivation of the metal occurs; 2) the rate of corrosion of the metal rises sharply when the layer at the electrode surface is rendered alkaline, which occurs, for example, in the corrosion of aluminum; 3) the slower stage in the anodic dissolution of metal is the diffusion of metal ions from the electrode; 4) other disturbances occur in the exponential relationship between the rate of the anodic process of dissolution of metal and the potential of the metal.

If the slowest stage in the anodic dissolution of metal is the diffusion of metal ions from the surface layer into the bulk of the solution, the rate of the anodic reaction of dissolution of metal, and therefore the rate of corrosion, will depend on the concentration of ferrous ions in the surface layer c_{Fe} in accordance with the equation:

$$i_a = k_p D c_{Fe}. \tag{21}$$

The concentration of metal ions in the bulk of the solution is zero. On the basis of the values of permissible corrosion losses we assume a value of i_{a_p} and determine the corresponding "protective" concentration of ferrous ions in the surface layer c_{Fe_p} from Equation (21). In its turn the concentration of metal ions in the surface layer is related to the potential of the metal by Equation (12), which in this case takes the form:

$$k_1 \cdot \exp \frac{\beta F}{RT} \varphi_p = k_2 c_{Fe_p} \exp \frac{-\alpha F}{RT} \varphi_p + k_p D c_{Fe_p}. \tag{22}$$

Solving the equation for φ_p, we obtain the value of the protective potential corresponding to our assumed permissible rate of corrosion i_{a_p}. The analytical solution of Equation 22 meets serious difficulties; it is expedient to solve it graphically.

In conclusion we express our deep indebtedness to Ya. M. Kolotyrkin and A. N. Frumkin for valuable suggestions made during the discussion of this work.

SUMMARY

1. Methods proposed by Harrel, Clerc, and Zhuk for the calculation of protective potentials were examined. It was shown that these methods are useless for the calculation of protective potentials.

2. A new method for calculating protective potentials is described. It is based on an exponential relationship between the rate of the anodic process of dissolution of metal and the potential.

3. The proposed method of calculating protective potentials of metals was verified for copper, zinc, cadmium, magnesium, lead, iron, and cast iron in 1.5% sodium chloride solution and for iron in artificial lake water. Close agreement between calculated and experimentally determined protective potentials was found.

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FORMATION OF CARBON DIOXIDE IN THE PREPARATION OF BUTADIENE FROM BUTANE – BUTENE MIXTURES

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In the dehydrogenation of butane, butene, or butane-butene mixtures over catalysts containing chromium oxide, considerable amounts of carbonaceous deposit are formed on the catalyst [1]. When the reaction mixture is diluted with steam [2], no appreciable carbonaceous deposit forms, but carbon dioxide, amounting to almost one half of the by-products, makes its appearance among the reaction products, so that investigation of the ways in which carbon dioxide may be formed acquires not only theoretical, but also practical importance. It would be of great interest to find out whether carbon dioxide is really a by-product of the dehydrogenation of butene, i.e., whether its formation proceeds in parallel with the formation of butadiene, or whether it is formed by the further transformation of butadiene.

The formation of a carbonaceous deposit on the catalyst in the dehydrogenation of butane was investigated by Blue and coworkers with the aid of radio-carbon [3]. The experiments were carried out at 550° with an addition of labeled butene. It was shown that, under the given conditions, the contribution of butane to the formation of the carbonaceous deposit was 25%, the formation of the remaining 75% being attributed by the authors to butene or butadiene.

We have investigated the way in which carbon dioxide is formed under the conditions for the dehydrogenation of butane-butene mixtures [4] at 635° over a chromium oxide catalyst with dilution of the reaction mixture with steam.

EXPERIMENTAL

If we examine a reaction scheme in which there is the possibility of the formation of carbon dioxide from two substances A_1 and A_2 having specific activities of α_1 and α_2:

$$A_1 \xrightarrow{w_1} CO_2 \xleftarrow{w_2} A_2$$

(in which w_1 and w_2 are the respective reaction rates for the conversion of A_1 and A_2 into CO_2), then with the aid of the isotope-kinetic method [5] we may determine the ratio of the rate constants w_1 and W_2.

The overall rate of formation of carbon dioxide will be:

$$\frac{dc_{CO_2}}{d\tau} = w_1 + w_2. \qquad (1)$$

Accumulation of radioactivity in the carbon dioxide will proceed by the same law:

$$\frac{dc^{*}_{CO_2}}{d\tau} = w^{*}_1 + w^{*}_2, \qquad (2)$$

in which $w_i^* = \alpha_i w_i$. Differentiating the equation $c^*_{CO_2} = \alpha_{CO_2} c_{CO_2}$ we obtain:

$$\frac{dc^*_{CO_2}}{d\tau} = \frac{d\alpha_{CO_2}}{d\tau} c_{CO_2} + \frac{dc_{CO_2}}{d\tau} \alpha_{CO_2}. \tag{3}$$

If the rates w_1 and w_2 for the catalytic reaction are expressed as follows [6]

$$w_1 = k_1' \frac{a_1 c_1}{1 + \Sigma a_i c_i} = k \frac{c_1}{1 + \Sigma a_i c_i}; \quad w_2 = k_2' \frac{a_2 c_2}{1 + \Sigma a_i c_i} = k_2 \frac{c_2}{1 + \Sigma a_i c_i}, \tag{4}$$

in which k_1' is the rate constant of the reaction, a_i are adsorption coefficients, and c_i are the corresponding concentrations of products, from Equations (2-4) we obtain the following expression for the specific activity of the carbon dioxide:

$$\alpha_{CO_2} = \frac{a_1 k_1 \frac{c_1}{1 + \Sigma a_i c_i} + a_2 k_2 \frac{c_2}{1 + \Sigma a_i c_i} - \frac{d\alpha_{CO_2}}{d\tau} c_{CO_2}}{k_1 \frac{c_1}{1 + \Sigma a_i c_i} + k_2 \frac{c_2}{1 + \Sigma a_i c_i}}. \tag{5}$$

This expression is greatly simplified if the specific activity varies little with time. We may then neglect the last term in the numerator of Equation (5) and obtained the following expression:

$$k_1 / k_2 = \frac{c_2 (a_2 - \alpha_{CO_2})}{c_1 (\alpha_{CO_2} - a_1)}. \tag{6}$$

Hence, for the determination of the ratio of rate constants for the formation of carbon dioxide from two substances it is necessary to know the ratio of the concentrations of these two substances and the specific activities of these substances and carbon dioxide. These values can be taken from the results of experiments on the dehydrogenation of a butane-butene-C^{14} mixture described in a previous paper [4], and the ratio of rate constants for the formation of carbon dioxide from butane and from butene can be determined. The necessary data are collected in Table 1.

TABLE 1

Specific Activities of Products per mM (percent on original activity of butane)
(The value for carbon dioxide is multiplied by the factor 4)

Experiment	τ (seconds)	Starting substance		Product				k_1/k_2
		C_4H_{10}	C_4H_8	C_4H_{10}	C_4H_8	C_4H_6	CO_2	
22	1.11	100	0	99.8	0.48	0.39	2.76	0.024
23	1.74	100	0	99.7	0.77	0.29	1.84	0.011
21	2.56	100	0	98.8	0.97	0.48	2.29	0.014
						Mean		0.016 ± 0.005

As the specific activities of butene and butadiene in these experiments were very similar and the ratio of the concentration of butane to that of butene + butadiene was close to unity, the ratio of the rate constants for the formation of carbon dioxide from butane and from butene + butadiene (given in Table 1) were determined

from the simplified equation:

$$k_1 / k_2 = \frac{\alpha_2 - \alpha_{CO_2}}{\alpha_{CO_2} - \alpha_1} . \qquad (7)$$

Hence, only about 1.5% of carbon dioxide was formed from butane under our conditions.

In the investigation referred to above [3], in which the dehydrogenation of butane (550°, without dilution with steam) in presence of added labeled butene was studied, it was found that the carbonaceous deposits on the catalyst were also formed mainly from butene (or butadiene), but the contribution of butane to the process was 25%. The cause of this discrepancy will be explained below.

The data of Table 1 are not yet sufficient for the separate determination of the contributions made by butene and butadiene to the formation of carbon dioxide. We can state only that these two hydrocarbons together give more than 98% of the carbon dioxide. For the determination of the relative contributions of butene and butadiene to the formation of carbon dioxide we made use of labeled butadiene.

As in a previous investigation [5], the experiments were carried out with a mixture of inactive butane and butene with an addition of butadiene labeled with radio-carbon, the relative amounts being 48.0, 50.3, and 1.7%, respectively. In order to avoid loss of butadiene by dissolution, the gas holder containing the original mixture was replaced by a large flask, from which the mixture was taken by means of a pump [7]. The experimental results are given in Table 2.

TABLE 2

Specific Activities of Products per mM (percent on original activity of butadiene)
(The value for carbon dioxide is multiplied by the factor 4)

Experiment	τ (seconds)	Starting substance			Product			
		C_4H_{10}	C_4H_8	C_4H_6	C_4H_{10}	C_4H_8	C_4H_6	CO_2
24	1.19	0	0	100	0	0.9	8.6	7.8
25	1.48	0	0	100	0	0.8	7.7	6.9
26	3.6	0	0	100	0	—	4.6	4.9

As will be seen, the specific activity of the carbon dioxide is close to that of the butadiene. Determination of the ratio of constants by the above-described method for butene (k_1) and butadiene (k_2) gave the value k_1/k_2 = 0.08 (for Experiments 24 and 25), which indicates that more than 90% of the carbon dioxide was formed from butadiene; the relative rate constants for the formation of carbon dioxide from butadiene, butene, and butane are 60 : 4 : 1. As will be seen, the ratio of the constants for the formation of carbon dioxide from butane and butene differ little from that obtained in the investigation [3] and the above-mentioned discrepancy can probably be explained by the substantial nonformation of butadiene under the conditions of dehydrogenation of butane.

Comparison of our results with those of the investigation [3] indicates that the formation of a carbonaceous film on the catalyst in absence of steam and the formation of carbon dioxide in presence of steam are related processes. In the second case steam either removes carbonaceous deposits or prevents their formation, oxidizing the corresponding intermediate products.

From the results of the determination of the relative rate constants for the formation of carbon dioxide in the process under consideration it can be seen that carbon dioxide formation proceeds not in parallel with the formation of butadiene, but results mainly from a secondary reaction of the decomposition of butadiene.

SUMMARY

1. The process by which carbon dioxide is formed in the dehydrogenation of butane-butene mixtures was investigated.

2. The relative rate constants for the formation of carbon dioxide from butane, butene, and butadiene were determined.

3. It was shown that carbon dioxide results mainly from the decomposition of butadiene.

4. It was shown that the process by which carbon dioxide is formed is allied to the process whereby carbonaceous deposits are formed on the catalyst when the reaction mixture is not diluted with steam.

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OXIDATION OF PARAFFIN INITIATED BY NITROGEN DIOXIDE

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The investigation of the oxidation of paraffin with atmospheric oxygen has been associated mainly with the very important practical problem of obtaining fatty acids containing 10-20 carbon atoms in their molecules. The possibility of carrying out such a process economically has been proved by the experience of several factories, which have used permanganates and manganese oxides as catalysts. However, the existing technological process is not free from serious defects, mainly associated with the necessity of introducing solid catalyst in the suspended condition into the system. In this connection it was considered that it would be of interest to bring about the oxidation of paraffin by the method, proposed by one of us [1], of gaseous initiation of liquid-phase chain reactions. In essence this method consists in the addition of gas catalyzing the oxidation process (NO_2, Cl_2, O_3, HBr, and others) to the air or oxygen entering the reaction vessel, addition being stopped after a certain period of reaction initiation and oxidation continued with air or oxygen in absence of catalyst. The effectiveness of the method of gaseous initiation was verified for the oxidation of decane and hexadecane with hydrogen bromide, nitrogen dioxide, and chlorine as initiators [2].

The present investigation had the object of studying the kinetics and chemistry of the oxidation of paraffin initiated by nitrogen dioxide. In this way an attempt was made to pass from the study of individual hydrocarbons to a complex hydrocarbon mixture, i.e., to a subject of immediate practical significance.

In the literature (particularly patent literature) there are reports of the oxidation of paraffin with nitric acid [3] and with air containing oxides of nitrogen [4, 5]. These investigations aimed at the replacement of atmospheric oxygen by more effective oxidants for paraffin, and they are chemical investigations of the final composition of the reaction products. Enler and Hasselquist [4] worked on the catalyzed oxidation of paraffin by air containing NO_2. Air containing 10% of NO_2 was passed continuously through molten paraffin at 130°. Ammonium vanadate was used as catalyst. After nine hours of reaction the product was found to contain 31.6% of hydroxy acids and dicarboxylic acids, 31.6% of fatty acids, and 36.8% of unhydrolyzable compounds. Under these conditions the oxidized paraffin was dark brown, which evidently indicated much resinification. As no results were given for the oxidation of paraffin with ammonium vanadate as catalyst but in absence of NO_2, it is impossible to judge what specific effect NO_2 had on the composition and yields of the oxidation products. The use of nitrogen dioxide, not as a constant addition to the air entering the oxidation reaction, but as a gaseous catalyst operating in the initiation period, was first studied and described by one of us in the above-cited papers [1, 2].

EXPERIMENTAL

As the substance to be oxidized we selected Kepsen paraffin (product of the German Democratic Republic). This contains 95% of normal paraffins and small amounts of branched and unsaturated hydrocarbons. We used atmospheric oxygen and sometimes pure oxygen as oxidizing agent. The oxidation was carried out in oxidation cells provided with glass filters for the distribution of air. A detailed description of the cell and the experimental procedure is given in the paper [6], which is devoted to the kinetics and chemistry of the oxidation of decane. Gaseous initiation of the oxidation process was effected by feeding air containing NO_2 for a definite time from the start of reaction. For this purpose NO was mixed into the stream of air. Nitric oxide was prepared by interaction of $FeCl_3$ and $NaNO_2$ solutions in presence of HCl, and it was collected over water in a gas holder. The rates of feed of air and NO were measured with flowmeters. The rate of feed of air was maintained constant at 20 liters/hour. It was shown by special experiments that increase in the rate beyond 10 liters/hour does not

produce any change in the yields of reaction products. Hence, the rate of feed of air in our experiments (20 liters/hour) was sufficiently high and we could neglect the slight consumption of oxygen in the oxidation of NO to NO_2 during the period of initiation. When the initiation process was complete, the nitric oxide feed was stopped and further oxidation was effected by atmospheric oxygen without any catalyst or initiator. All experiments (except those in which a variable temperature was used) were carried out at a constant temperature of 127°.

The oxidized paraffin was analyzed for peroxides, carbonyl compounds, alcohols, acids, and esters. Weighed samples of paraffin, taken at definite intervals of time after the start of reaction, were dissolved in a mixture of gasoline and alcohol. Peroxides were determined in two ways: chemically and polarographically. Iodometric determination of peroxides was carried out by addition of a mixture of 1 ml of chloroform, 1 ml of acetic acid, and 2 ml of a saturated alcoholic solution of potassium iodide to a test sample (0.4 g of oxidized paraffin). Nitrogen or carbon dioxide was passed through the resulting solution in order to remove dissolved oxygen, and the mixture was then left for one day in the dark. The liberated iodine was then titrated with 0.01 N $Na_2S_2O_3$.

In the literature on polarographic procedures there are references to the possibility of the polarographic determination of organic peroxides in nonaqueous media [7, 8]. In the present work, as solvent for the oxidized paraffin in polarographic analysis we used a mixture of benzene and methanol (3 : 1) containing 0.1 of an equivalent of lithium chloride per liter. This mixed solvent served, at the same time, as a supporting electrolyte for the electroreduction of the peroxides. In order to remove dissolved oxygen, before the start of reduction hydrogen was passed through the solution in the electrolytic vessel for 30 minutes. After this treatment polarograms of the supporting electrolyte showed no waves that would interfere with the determination of peroxides. Graduation of the capillary for the quantitative determination of peroxides was carried out with solutions of hydrogen peroxide of known concentration.

A typical polarogram of such a solution with a supporting electrolyte of 0.1 N LiCl is shown in Fig. 1. In the same figure we give the polarogram of a solution of a test sample of oxidized paraffin (Curve 2). As will be seen, there are well-defined waves of identical half-wave potential (−0.85 v) in both cases, which indicates the identity of the peroxy groups in the two test samples.

Alcohols were determined in the form of the corresponding nitrites [9]. With this object, 0.2 ml of 5 N HCl and 0.5 ml of 25% $NaNO_2$ solution were added to a solution of a sample of the oxidized paraffin in 5 ml of gasoline, previously purified with sulfuric acid and distilled over the range 50-115°. The nitrous ester formed passed into the gasoline layer, which was separated from the aqueous layer, washed free from oxides of nitrogen with 0.1 N NaOH, and examined on an SF-4 spectrophotometer for its absorption at 360 mμ.

Carbonyl compounds were determined with the aid of a 5% solution of hydroxylamine hydrochloride in ethanol. The mixture was heated for ten minutes in a water bath, and the HCl liberated was titrated with 0.1 N alcoholic alkali in presence of Bromphenol blue at − 50° to − 70° (titration at low temperature results in a sharper end point). Acids were determined by titration with 0.1 N alcoholic alkali in presence of phenolphthalein. Esters were determined by hydrolysis of a sample with excess of 1 N alcoholic alkali for one hour in a water bath followed by titration of excess of alkali with 0.1 N HCl in presence of phenolphthalein. In the determination of esters account was taken of the amount of acids present in the sample being analyzed.

It should be noted that nitrogen dioxide introduced during the initiation period did not interfere in any of the above-described determinations, neither in the form of nitrogen dioxide itself nor in the form of any compound derived from it. The maximum amount of NO_2 taken was 10^{-4} mole in the usual test sample of oxidized product (0.4 g), which is within the limits of the error of chemical analysis. In the polarographic analysis it was shown by special experiments that, after the passage of air containing the maximum amount of NO_2 used in our experiments through the paraffin at 127°, no waves were to be observed on the polarograms of the paraffin. In just the same way, in a sample taken immediately after the initiation there was no absorption at 360 mμ.

The analysis was expressed in the generally accepted conventional units: peroxide, carbonyl, alcohol, acid, and ester values. The peroxide value was generally expressed as the percentage of iodine liberated in the reaction of peroxides contained in 1 g of sample with potassium iodide. Acid and carbonyl values were expressed as the number of milligrams of KOH required in the titration of a 1-g sample (in the case of carbonyl values, in the titration of HCl formed by reaction with hydroxylamine hydrochloride). The ester value was expressed as the number of milligrams of KOH required for the hydrolysis of the esters present in a 1-g sample. The

determination of alcohols in the paraffin was generally carried out by the acetylation method and, correspondingly, alcohol (acetyl) values were expressed as the number of milligrams of KOH required for the neutralization of acetic acid formed in the hydrolysis of the acetylated product. In the spectrophotometric analysis, the concentration of alcohol was determined by comparison of the absorption of the solution at 360 mμ with that of the solutions of known concentration used in the prior calibration. In our case the graduation was carried out with butyl alcohol, and alcohol values are given in units based on this alcohol.

Experimental Results and Discussion of Results

The oxidation of paraffin in absence of catalysts and initiators is characterized by a very long period of induction during which no appreciable change in the composition of the reaction mixture can be detected. Thus, under the conditions of our experiments in the oxidation of Kepsen paraffin with atmospheric oxygen at 127°, there is an induction period of 366 hours. Application of the method of gaseous initiation in the oxidation of paraffin leads to qualitatively new results. Thus, the first experiments showed that, if the paraffin to be oxidized is treated with air containing 10% of NO_2 for a period of only one minute at the beginning of the reaction period and further oxidation is carried out with NO_2-free air, the induction period is shortened from 366 hours to 8-10 hours. At the end of the induction period, both in the case of uncatalyzed oxidation and also in the case of initiation with NO_2, an autoaccelerated process of oxidation of the paraffin with formation of peroxides, alcohols, carbonyl compounds, acids, and esters begins.

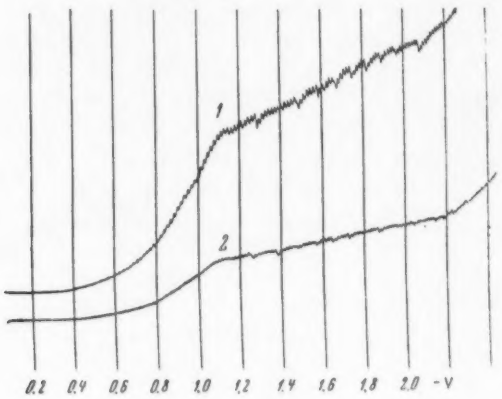

Fig. 1. Polarograms of the electroreduction of hydroperoxides from decane (Curve 1) and of peroxides formed in the oxidation of paraffin initiated for a period of 30 minutes by air containing 0.35% of NO_2 (Curve 2).

The effect of gaseous initiation is clearly demonstrated by the kinetic curves for the accumulation of acids presented in Fig. 2. In Fig. 2 and succeeding figures concentration of acids is expressed as acid values. Curve 1 represents the kinetics of the formation of acids in the noninitiated oxidation of paraffin, and Curve 2 represents the formation of acids in the oxidation of paraffin initiated for a period of one minute by nitrogen dioxide. In both cases atmospheric oxygen was used as oxidant. If the oxidation is effected with pure oxygen instead of air then, other things being equal, the period of induction for the oxidation of paraffin is shortened still further (Fig. 2, Curve 3).

An examination of the kinetic curves for the formation of acids (Fig. 2) indicates that in initiation by NO_2 reaction comes to a stop when an acid value of about 45 is attained, no further formation of acids occurring in spite of the fact that a sufficient amount of paraffin is present for reaction. Hence, nitrogen dioxide has a dual effect on the oxidation of paraffin: on the one hand it favors the oxidation, greatly shortening the induction period, and on the other hand it has a harmful effect, lowering the yields of reaction products (in particular, acids). The limiting yield of acids is greatly dependent on the NO_2 content of the air and on the time for which

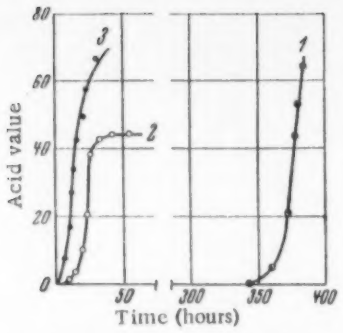

Fig. 2. Kinetics of the formation of acids in the oxidation of paraffin at 127°: 1) uncatalyzed oxidation (air); 2) oxidation by air initiated for 1 minute (10% of NO_2 in air); 3) oxidation by oxygen initiated for 1 minute (10% of NO_2 in oxygen).

air containing NO_2 is allowed to take part in the oxidation (period of initiation).

In order to characterize the initiating effect of nitrogen dioxide quantitatively, two series of experiments were carried out: in one of these kinetic curves for the formation of acids were measured for different periods of initiation but for a constant NO_2 content of the air (10% NO_2, Fig. 3; 0.35% NO_2, Fig. 4); in the other the NO_2 content of the air was varied and the period of initiation was maintained constant at 30 minutes (Fig. 5). It will be seen from Figures 3-5 that it is sufficient to introduce very small amounts of NO_2 during the initiation period in order to shorten the induction period for the oxidation of paraffin considerably. Thus, with passage of air containing only 0.11 % of NO_2 for the first 30 minutes, the induction period is shortened from 366 hours to 35 hours, and with initiation by air containing 0.35% of NO_2 for seven minutes the period is shortened to 55 hours. With increase in the NO_2 content of the air in a 30-minute period of initiation and with lengthening of the period of initiation at constant NO_2 content of the air, the period of induction becomes shorter. However, the effectiveness of extra NO_2 is reduced as the NO_2 content increases, and finally further increase in the NO_2 content of the air does not result in further shortening of the induction period. Thus, for a 30 - minute initiation period the induction period is not affected by increase of NO_2 content in the range 5-10% (Fig. 5). Similarly, for an NO_2 content of 0.35% (Fig. 4), almost the same induction period was observed for initiation periods of 30, 60, and 120 minutes.

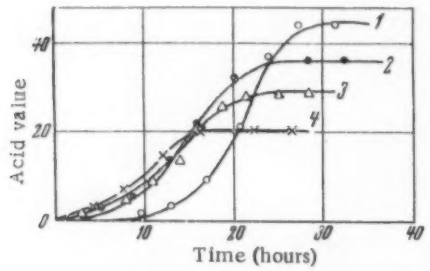

Fig. 3. Kinetics of the formation of acids in the oxidation of paraffin initiated by NO_2 (0.35% NO_2 in air, 127°) for : 1) 1 minute; 2) 5 minutes; 3) 10 minutes; 4) 30 minutes.

It was of interest to compare the results of these two series of experiments in order to determine whether the initiating action of NO_2 is simply a function of the amount of NO_2 taken in the reaction irrespective of the rate of feed of NO_2. The relation between the induction period and the total amount of nitrogen dioxide passed through the paraffin is represented in Fig. 6 in semilogarithmic coordinates. The black points (•) refer to experiments carried out at a constant NO_2 concentration (0.35%) in the air, and the others (o) refer to a constant period of initiation (30 minutes). It will be seen from Fig. 6 that the induction period is shortened (within the limits indicated above) with increase in the total amount of NO_2 passed through the paraffin during the initiation period, irrespective of whether initiation is for a short time with a high NO_2 content of the air or for a longer time with a lower NO_2 content.

As regards the limiting yields of acids, no such relationship is observed. The limiting yields of acids are substantially dependent on the schedule of the initiation process. Figure 7, which represents the relation of the maximum yield of acids to the NO_2 concentration and to the initiation period, indicates that it is more advantageous to carry out initiation at low NO_2 concentrations (0.2-0.4%) than at concentrations of 5-10%. The initiation period is then determined by the optimum amount of NO_2 for the shortening of the induction period; this will permit a fairly high yield of acids.

The unfavorable effect of high additions of nitrogen dioxide on the oxidation of paraffin is most graphically demonstrated by experiments in which air containing NO_2 is continuously passed through the paraffin being oxidized. With this procedure the yield of fatty acids is extremely low and the oxidized product is dark brown

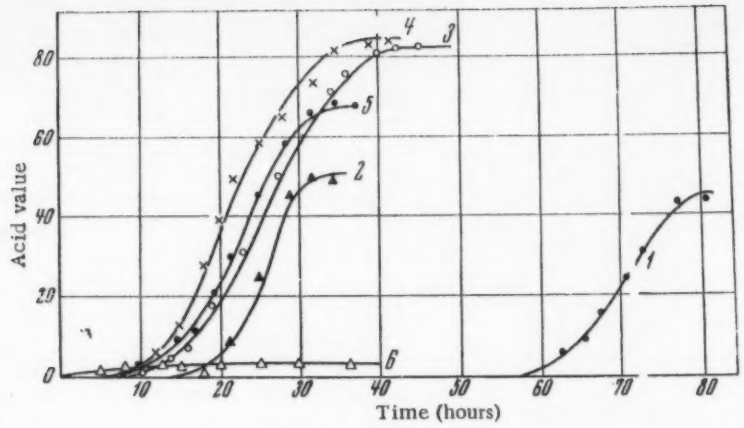

Fig. 4. Kinetics of the formation of acids in the oxidation of paraffin initiated by NO_2 (0.35% NO_2 in air, 127°) for: 1) 7 minutes; 2) 10 minutes; 3) 30 minutes; 4) 60 minutes; 5) 120 minutes; 6) with continuous feed of NO_2.

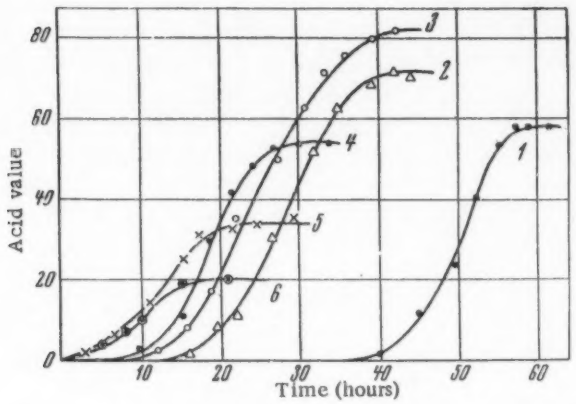

Fig. 5. Kinetics of the formation of acids in the oxidation of paraffin initiated by NO_2 for 30 minutes (127°) at an NO_2 content in the air of : 1) 0.11%; 2) 0.2%; 3) 0.35%; 4) 1.0%; 5) 5.0%; 6) 10%.

and appears to contain a large amount of products of the resinification of the paraffin. When there is a continuous feed of NO_2 (Fig. 4), the formation of acids ceases at the very beginning of the reaction. It is probably to this unfavorable action of NO_2 that we must attribute the great darkening of the solution observed in the experiments of Enler and Hasselquist [4] cited above. With the object of intensifying the oxidation process, these authors used a constant feed of NO_2, a method which, as the present work has shown, is unsatisfactory. We have not yet obtained sufficient data to enable us to explain the lower yields of acids in presence of large additions of NO_2. We cannot exclude the possibility that this effect is associated with the accumulation of certain intermediate or final products in the reacting mixture. Since water is known to lower the rate of oxidation of some hydrocarbons in the liquid phase [10], we have suggested that it also may be one of the reaction products inhibiting the formation of acids in the oxidation of paraffin. We therefore carried out experiments designed to determine the effect of additions of water on the oxidation of paraffin under our conditions.

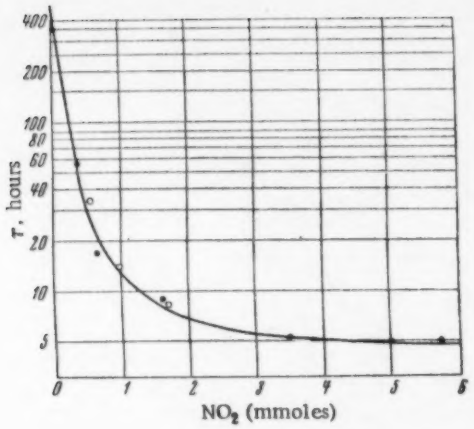

Fig. 6. Relation between induction period and amount of NO_2 passed through the paraffin during the initiation period: •) for 0.35% NO_2 in the air and different induction periods; o) for a 30-minute initiation and different NO_2 contents in the air. Temperature 127°.

Paraffin was saturated with water (molten paraffin was shaken with water, and the paraffin was then separated in a separating funnel) and oxidized by the method of gaseous initiation. The induction period for the oxidation of paraffin treated in this way was found to be longer and the limiting yield of acids lower than for dry paraffin oxidized under the same conditions. The following experiment was then carried out. Oxidation of paraffin initiated by nitrogen dioxide for 30 minutes (5% of NO_2 in the air) was discontinued when an acid value of 30 mg was attained. Under these conditions the maximum yield of acids corresponds to an acid number of 40 mg. The oxidized product was removed from the reaction vessel and divided into two parts: the first was dried in a desiccator over calcium chloride for seven days, and the second was kept in an open vessel. Both parts were then subjected to oxidation under identical conditions without further initiation. The oxidation of that part of the paraffin which was not dried was resumed at the same rate as that occurring when oxidation was discontinued and the kinetic curve for the formation of acids (Fig. 8, Curve 1, points denoted by "o") coincided exactly with that for a control experiment in which reaction was not stopped (Curve 1, points denoted by "•"). On the other hand, the yield of acids in the oxidation of the dried paraffin was considerably higher (Curve 2). These experiments indicate that water is indeed one of the reaction products that retard oxidation of the

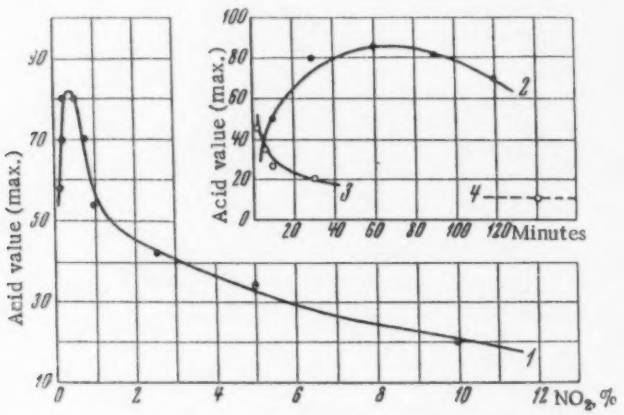

Fig. 7. Maximum yields of acids in the oxidation of paraffin initiated by nitrogen dioxide: 1) as a function of NO_2 concentration for a 30-minute initiation; 2) as a function of the initiation period for 0.35% NO_2; 3) as a function of the initation period for 10% NO_2; 4) for continuous initiation with 0.35% NO_2.

paraffin and lower the yield of acids. However, the observed effect of retardation and stopping of the reaction cannot be attributed entirely to the action of water; some part is probably played by other reaction products, particularly substances containing NO_2 or formed with the participation of NO_2.

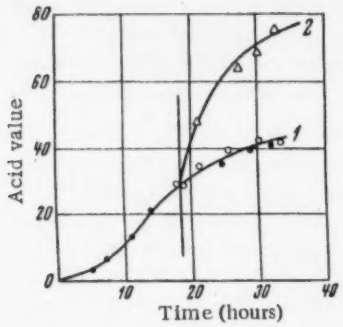

Fig. 8. Effect of water on the kinetics of the formation of acids in the oxidation of paraffin initiated by 5% of NO_2 in the air for 30 minutes at 127°: 1) control experiment (•) without a break in the reaction; and continuation of oxidation after a break (after 18.5 hours) without drying of the paraffin (o); 2) continuation of oxidation after the break with intermediate drying of the paraffin.

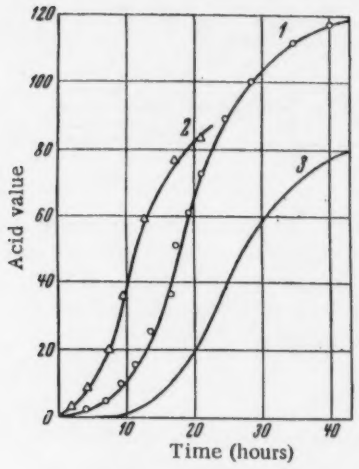

Fig. 9. Kinetics of the formation of acids in the oxidation of paraffin with a variable-temperature schedule of initiation (0.35% of NO_2 in the air, initiation period 30 minutes): 1) 150° for first 40 minutes and then 127° to end of reaction; 2) 150° for first two hours and then 127°; 3) constant temperature of 127° (the curve is transferred from Fig. 4 without points)

Hence, the results of experiments with variation of the initiation period (right up to continuous feed of NO_2) and of NO_2 content of the air indicate that the detailed procedure of gaseous initiation has a considerable effect on the oxidation process. Another factor in the initiation process is temperature. Rise in reaction temperature during the initiation period (and also for a somewhat longer time) has a favorable effect on the formation of acids. Experiments with a variable-temperature schedule were carried out for a 30-minute initiation at an NO_2 content of 0.35% in the air, i.e., under optimum conditions for the formation of acids. The results of these experiments are presented in Fig. 9. Curve 1 is the kinetic curve for the formation of acids when the reaction temperature is maintained at 150° for the first 40 minutes of the process (which includes the initiation period), after which it is quickly lowered to 127° (the vessel is transferred to another thermostat). Curve 2 represents the kinetics of the formation of acids under the same conditions, but a temperature of 150° is maintained for the first 90 minutes of the reaction. For comparison, the kinetic curve for the formation of acids under constant-temperature conditions (127°) is also given in Fig. 9 (Curve 3). It is quite evident from these curves that elevation of temperature at the beginning of the process results both in further shortening of the induction period and in increase in rate of oxidation and rise in the maximum yields of acids.

In all experiments considered so far, the kinetics of the oxidation of paraffin initiated by nitrogen dioxide have been studied by reference to the accumulation of a final reaction product, fatty acids. We carried out also a separate series of experiments in which the reaction products were analyzed for their contents of peroxides, carbonyl compounds, alcohols, and esters. The kinetic curves for the formation of these products are given in Figures 10 and 11. The kinetic curve for the formation of peroxides (Fig. 10), as would be expected from the fact that peroxides form an intermediate product in the reaction, passes through a maximum. The accumulation of alcohols, carbonyl compounds, and esters, like that of acids, follows an autocatalytic law, but from a certain moment in the reaction (about 30 hours) the formation of these reaction products ceases.

As already stated in the description of experimental procedure, peroxides were determined by two methods-chemical and polarographic. In this way we obtained interesting results on the composition of the peroxides

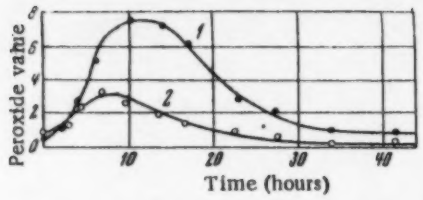

Fig. 10. Kinetics of the formation of peroxides in the oxidation of paraffin initiated with NO_2 for 30 minutes (NO_2 content of air 0.35%) at 127° : 1) according to chemical analysis; 2) according to polarographic analysis.

formed in the oxidation of paraffin. The polarograms of oxidized decane (and also isodecane) containing peroxides are identical with polarograms of solutions of oxidized paraffin (see Fig. 1). In all cases a well marked wave was obtained at a half-wave potential of − 0.85 v for the reduction of peroxides. Such a reduction potential is characteristic for solutions of various hydroperoxides in nonaqueous solvents.

In the investigation [8] it was shown that the hydroperoxide group is reduced at a dropping mercury electrode at a half-wave potential of − ~ 0.8 v* with preservation of the same relation between peroxide concentration and diffusion current irrespective of the structure of the remainder of the molecule (tert-butyl hydroperoxide, hydroperoxides of tetralin, cumene, pinene, and others). Peroxides not containing the hydroperoxide group are not reduced under these conditions. Hence, the quantitative characterization of the hydroperoxides formed in the oxidation of paraffin by the height of the − 0.85 v wave is quite reliable.

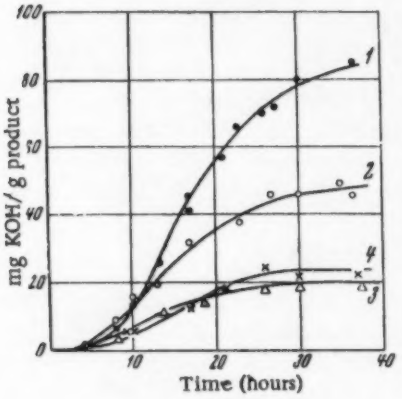

Fig. 11. Kinetics of the formation of 1) acids; 2) carbonyl compounds; 3) alcohols; 4) esters in the oxidation of paraffin initiated for 30 minutes at 127° with NO_2 (NO_2 content of air 0.35%).

Figure 10 gives kinetic curves for the formation of peroxides constructed from data derived from chemical (Curve 1) and polarographic (Curve 2) analyses of the oxidized paraffin. Examination of these curves shows that the total peroxide content as determined iodometrically greatly exceeds the amount of peroxides indicated by the polarographic method. This indicates that the peroxides formed in the oxidation of paraffin are not homogeneous in composition. At least two types of peroxides are formed in the reaction − one of these (hydroperoxides) is reduced at a dropping mercury electrode, and the other is not determined in polarographic analysis. A similar discrepancy between the results of chemical and polarographic analysis for peroxides was observed also in the oxidation of methyl linoleate [11]. However, in papers devoted to the oxidation of saturated hydrocarbons, this fact has not previously been reported.

Returning to our examination of the kinetic curves (Fig. 10), we must point out a fact of interest from the point of view of the oxidation mechanism: in the first stage of the reaction − in the course of the first six hours − the amounts of peroxides found by the two methods are almost identical. This indicates that the primary oxidation product of paraffin probably consists of hydroperoxides. Later, however, peroxides of another structure appear, and their appearance in the later stages of the reaction indicates the secondary character of these reaction products.

Surprising results were obtained in the determination of peroxy compounds in the original paraffin. As will be seen from Fig. 10, the original paraffin contained appreciable amounts of peroxides (about 0.5%). As the uninitiated oxidation process develops extremely slowly in spite of the appreciable amount of peroxides in the system, we must suppose that the peroxides that can be detected in the original paraffin are not responsible for a branching-chain reaction. Hence, the peroxy compounds that break down to give radicals able to give rise to new oxidation chains are formed only as a result of oxidation of paraffin initiated (in our case) by nitrogen dioxide.

* As in original − Publisher's note.

SUMMARY

1. The use of the method of gaseous initiation of liquid-phase chain reactions, consisting in addition of nitrogen dioxide to the air for a short time at the beginning of the reaction, makes it possible to shorten the induction period for the oxidation of paraffin considerably. With a 30-minute initiation by air containing 0.35% of NO_2, the induction period is ten hours, as compared to 366 hours in absence of initiator.

2. Greater additions of NO_2 have an unfavorable effect on the oxidation process, reducing the maximum yields of acids. When there is a continuous feed of NO_2, acids are not formed in appreciable amount.

3. It was shown that water formed in the reaction has an inhibiting effect on the maximum yields of acids and increases the induction period for the oxidation of paraffin initiated by nitrogen dioxide.

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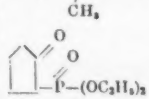
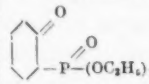
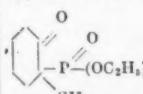
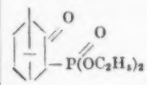
β - KETO PHOSPHONIC ESTERS

COMMUNICATION 2. ESTERS OF THE AROMATIC AND CARBOCYCLIC SERIES

B. A. Arbuzov and V. S. Vinogradova

In previous communications we described the syntheses of various β-keto phosphonic esters [1, 2] and investigated them by the bromine-titration method [3] with the object of determining whether keto-enol tautomerism is to be found in these phosphorus derivatives and also of demonstrating the analogy between these compounds and the corresponding carboxylic compounds, the keto-enol tautomerism of which has been studied fairly thoroughly. The results of chemical investigation and study of the ultraviolet absorption spectra [2, 4] indicated absence of enolization in phosphonoacetic and 2-phosphonopropionic esters, as in the case of malonic ester, and insignificant enolization in acetonyl- and 1-methylacetonyl-phosphonic esters, which are phosphorus analogs of acetoacetic ester and its methyl derivative.

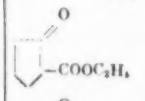
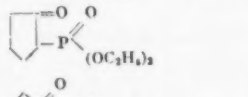
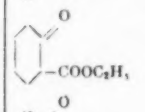
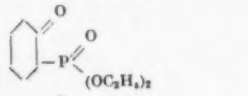
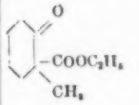
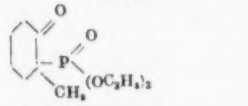
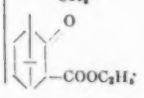
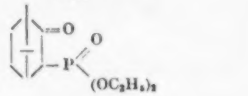
TABLE 1

No.	Formula of substance	B.p. in °C (p in mm)	n_D^{20}	d_0^{20}	MR Found	MR Calculated	Method	Yield (%)
1	$C_6H_5COCH_2P(OC_2H_5)_2$	170—173 (2.5)	1.5120	1.1650	66.01*	64.89	A	84
		165 (5.0)	1.4990	1.1615	64.79	64.89	B	36
2	$C_6H_5COCH(CH_3)P(OC_2H_5)_2$	156.5—158 (1.5)	1.5075	1.1328	71.00*	69.51	A	65
3	$C_6H_5COC(CH_3)P(OC_2H_5)_2$	137—138.5 (1.0)	1.4990	1.1052	75.53*	74.13	A	75
4		104—105 (1.0)	1.4560	1.1408	52.48	52.61	B	32
5		146—147 (8)	1.4595	1.1234	57.06	57.23	B	—
6		118—120 (1.0)	1.4565	1.0860	62.19	61.73	A	83.7
		119.5—121.5 (1.0)	1.4675	1.0902	63.26	61.73	B	36.5
7		116—116.5 (0.5)	1.4600	1.0842	72.81	73.40	B	59

* An analogous exaltation is found for benzoylacetic ester.

In the present communication we report the results of a study of acetonylphosphonic ester and its derivatives and also of some carbocyclic β-keto phosphonic esters. Phenacylphosphonic esters are interesting because the analogous benzoylacetic ester is much more enolized than acetoacetic ester. From this point of view 3-camphorylphosphonic ester and the phosphorus analogs of oxocyclopentane- and oxocyclohexane-carboxylic esters are of interest since the carboxylic compounds are enolized in various degrees. With this in view we synthesized various β-keto phosphonic esters, some already known and others not previously described in the literature. These compounds are listed in Table 1.

TABLE 2

No.	Formula of substance	Amount of enol (%)	Formula of substance	Unsaturation (%)	Method
1	$C_6H_5-CO-CH_2-COOC_2H_5$	21.4	$C_6H_5-CO-CH_2-P(O)(OC_2H_5)_2$	9.1	A
		—	$C_6H_5-CO-CH_2-P(O)(OC_2H_5)_2$	7.2	B
2	$C_6H_5-CO-CH(CH_3)-COOC_2H_5$	—	$C_6H_5-CO-CH(CH_3)-P(O)(OC_2H_5)_2$	3.0	A
3	$C_6H_5-CO-C(CH_3)_2-COOC_2H_5$	—	$C_6H_5-CO-C(CH_3)_2-P(O)(OC_2H_5)_2$	0	A
4		4.6		5.0	B
5		74.0		7.7	B
6		—		10	A
7		0.5		1.1	B

Diethyl phenacylphosphonate was first prepared by Arbuzov and Razumov by the action of triethyl phosphite or sodium diethyl phosphite on 2-bromoacetophenone [5]. We prepared diethyl phenacylphosphonate and its α- alkyl and α,α-dialkyl derivatives by the Arbuzov rearrangement: the action of the corresponding α-halo carbonyl compounds on triethyl phosphite (Method A). As the hydrogens of the methylene group of diethyl phenacylphosphonate were replaced by methyl radicals, in spite of the rise in molecular weight there was a lowering of boiling point similar to that found for phosphonoacetic ester [1], but still greater in magnitude. In the present case in each replacement of hydrogen by methyl the boiling point fell by more than 10°.

When the experiments of Arbuzov and Razumov [5] on the preparation of diethyl phenacylphosphonate by the action of sodium diethyl phosphite on 2-bromoacetophenone (Method B) were repeated, we obtained a substance that boiled 10-12° lower than the diethyl phenacylphosphonate obtained from triethyl phosphite. Diethyl 2-oxocyclopentylphosphonate and diethyl 3-camphorylphosphonate were prepared by the action of sodium diethyl phosphite on 2-chlorocyclopentanone and 3-bromocamphor respectively (Method B). Triethyl phosphite does not react with 3-bromocamphor, even at 220°. Diethyl 1-methyl-2-oxocyclohexylphosphonate was synthesized by the action of triethyl phosphite on 2-chloro-2-methylcyclohexanone (Method A). Reaction between sodium diethyl phosphite and 2-chloro-2-methylcyclohexanone gave the ester in low yield (Method B).

The synthesized compounds were studied by Meyer's classical bromine-titration method – the use of excess of bromine in conjunction with 2-naphthol [6]. The results are given in Table 2, in which, for comparison, data are given of enol contents determined by the same method for carboxylic compounds of analogous structure.

Comparison of the data in Table 2 shows that the enol content of diethyl phenacylphosphonate (9.1%) is less than that of the analogous ethyl benzoylacetate (21.4%). 2-Ethylbenzoylacetic ester, however, is weakly enolized (4%), and α-methylphenacylphosphonic ester is also weakly enolized and is enolized to a much lower extent than phenacylphosphonic ester. As would be expected, diethyl α,α-dimethylphenacylphosphonate does not react with bromine. An examination of the results of the bromine titrations of phenacylphosphonic ester and its derivatives, and also of phosphonoacetic ester, acetonylphosphonic ester, and derivatives of the latter reported previously [2, 3], enables us to conclude that there is an analogy between the enolization of β-keto carboxylic esters and that of their phosphorus analogs, the difference being that β-keto phosphonic esters enolize to a somewhat smaller extent. However, the parallelism is not complete. 2-Oxocyclopentanecarboxylic ester (No. 4) and 2-oxocyclohexanecarboxylic ester (No. 5) differ considerably in enol content, but 2-oxocyclopentyl- and 2-oxocyclohexyl-phosphonic esters do not show such a marked difference (5 and 7.7% of enol). There is a particularly marked difference in enolization between 2-oxocyclohexanecarboxylic ester (74%) and 2-oxocyclohexylphosphonic ester (7.7%). It must be noted, however, that the titration of 2-oxocyclohexylphosphonic ester does not go smoothly and does not give very definite results.

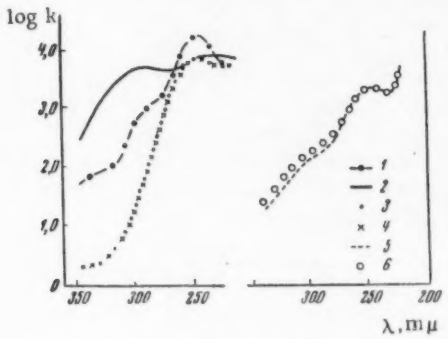


Fig. 1. Absorption spectra of solutions in methanol: 1) diethyl phenacylphosphonate (Method A); 2) diethyl phenacylphosphonate at $c = 8.6 \cdot 10^{-4}$ with addition of CH_3ONa at $c = 4.4 \cdot 10^{-2}$; 3) diethyl α,α-dimethylphenacylphosphonate; 4) diethyl α,α-dimethylphenacylphosphonate with addition of one equivalent of CH_3ONa; 5) diethyl phenacylphosphonate (Method B); 6) diethyl phenacylphosphonate (Method B) at $c = 1.8 \cdot 10^{-3}$ with addition of CH_3ONa at $c = 3.4 \cdot 10^{-2}$.

3-Camphorcarboxylic ester (No. 7) and 3-camphorylphosphonic ester are enolized to about the same very slight extent.

With the exception of the phenacylphosphonic and α-methylphenacyl-phosphonic esters, which were prepared by the Arbuzov rearrangement, all the investigated compounds gave no coloration in alcoholic solution with ferric chloride. Phenacylphosphonic ester gave a brownish-orange coloration, and α-methylphenacylphosphonic ester gave a more feeble but similar coloration.

This chemical characterization of the keto-enol tautomerism of organophosphorus compounds containing a carbonyl or carboxy group in the β-position to the phosphonic group was supplemented by a study of ultraviolet absorption spectra. Apart from its value in the study of the presence of keto and enol forms in the phosphorus analogs of β-keto carboxylic acids, the investigation of absorption spectra is of interest for its own sake since the available data on the absorption spectra of organophosphorus compounds are few: Milobendzki [7]

studied the absorption spectra of some phosphorous esters and of diethyl ethylphosphonate; Halmann [8] has given the spectrum of triethyl phosphite; Malatesta and coworkers [9] have provided data on the spectra of tripropyl phosphite and dipropyl hydrogen phosphite; and there are data also on the absorption spectra of arylphosphonic [10] and arylphosphonous [11] acids.

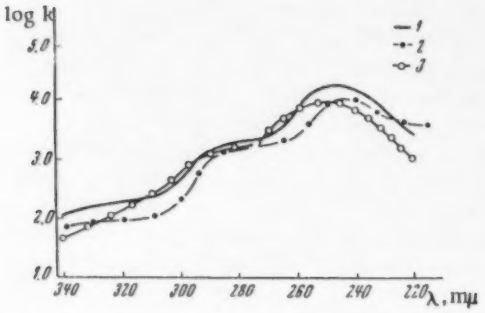


Fig. 2. Absorption spectra of diethyl phenacylphosphonate prepared by Method A: 1) in methanol; 2) in hexane; 3) in water.

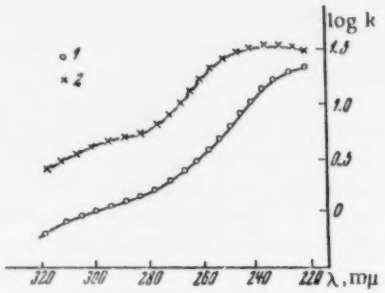


Fig. 3. Absorption spectra of diethyl 2- oxocyclopentylphosphonate: 1) in methanol; 2) in methanol with addition of one equivalent of CH_3ONa.

The absorption spectra were determined on an SF4 quartz spectrophotometer in absolute methanol, or sometimes without solvent or in hexane. In the study of keto-enol tautomerism investigators have frequently had recourse to the determination of absorption spectra in various solvents and in alkaline solutions such as alcoholic solutions of alkoxides. In the last case, when enolization occurred the equilibrium was greatly displaced in the direction of the formation of enol ions, which had an effect on the absorption spectra [12]. We therefore also determined absorption spectra in sodium methoxide solution.

Figure 1, Curve 1, gives the spectrum in methanol solution of diethyl phenacylphosphonate prepared by Arbuzov rearrangement. The spectrum has three maxima in the regions 2420, 2800, and 3200 A and is an almost exact repeat of the spectra of acetophenone and 2,2-dimethyl-1-phenyl-1,3-butanedione, which indicates the dominating effect of the benzoyl group on the absorption spectrum. The maximum at 3200 A is attributable to the carbonyl group, 2800 A to a carbonyl group as affected by a phenyl radical, and 2420 A to a phenyl group as affected by the attached carbonyl [13].

Comparison of the absorption spectrum of diethyl phenacylphosphonate with that of the α, α-dimethylphenacylphosphonic ester (Curve 3), for which enolization is impossible, indicated that the phenacylphosphonic ester is somewhat enolized. Diethyl α,α-dimethylphenacylphosphonate is characterized by greater absorption at 2450 A (keto form) and it shows no maximum at 2850 A (enol form).

Study of the absorption spectra of diethyl phenacylphosphonate and diethyl α,α-dimethylphenacylphosphonate in sodium methoxide solutions showed that the α,α-dimethyl compound gave identical spectra in alcohol and in alcoholic sodium methoxide (Curves 3 and 4). In the case of diethyl phenacylphosphonate (Curve 2) and diethyl α-methylphenacylphosphonate, the absorption of solutions in alcoholic sodium methoxide was greater in the region 2850-3200 A and less at 2450 A. In the case of benzoylacetic ester excess of sodium ethoxide also caused great increase in absorption in the region of 3060 A, which has been ascribed to a chelate sodium derivative of the enol form [13]. It may be supposed that the increase in absorption in the region 2850-3200 A in the case of phenacylphosphonic ester can be ascribed to the formation of enol anions or chelate compounds.

The enolization of phenacylphosphonic ester in alcoholic solution in presence of sodium methoxide is shown by absorption spectra to be somewhat greater than that of α-methylphenacylphosphonic ester. As in the case of acetonylphosphonic ester, hexane does not affect the absorption curve of phenacylphosphonic ester to an appreciable extent. In aqueous solution the absorption of phenacylphosphonic ester is somewhat less in the region of 2850 A (Fig. 2). However, there are data which indicate that the effect of solvent is not always present.

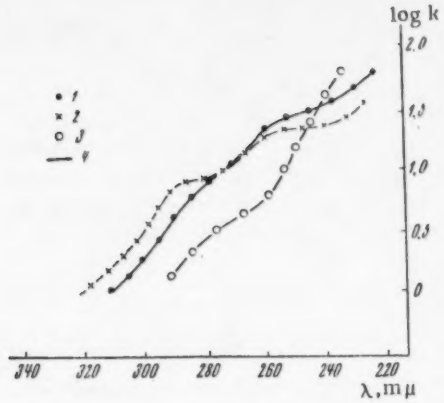


Fig. 4. Absorption spectra of methanol solutions: 1) diethyl 2-oxocyclohexylphosphonate; 2) diethyl 2-oxocyclohexylphosphonate with addition of one equivalent of CH_3ONa; 3) diethyl 1-methyl-2-oxocyclohexylphosphonate (Method A); 4) diethyl 1-methyl-2-oxocyclohexylphosphonate with addition of one equivalent of CH_3ONa.

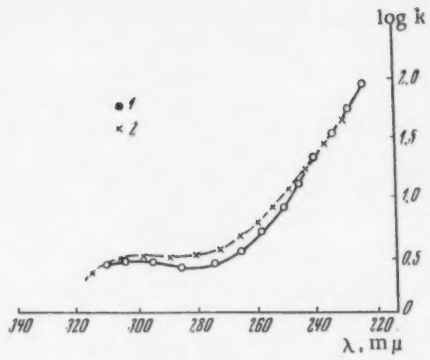


Fig. 5. Absorption spectra of diethyl 3-camphorylphosphonate in methanol solution: 1) with no addition; 2) with addition of one equivalent of CH_3ONa.

Thus, the enol content of ethyl 2-sec-butylacetoacetate is 9-9.5% in alcohol, 8.6-9.9% in hexane, and 8.5% in the liquid state. The enol content of 2-isopropylacetoacetic ester is 5% in the liquid state and 6% in hexane [14]. For keto-enol tautomers which do not form internal hydrogen bonds, the solvent effect is reversed: water enolizes and hexane ketonizes such compounds [15].

The spectrum of phenacylphosphonic ester synthesized by the action of sodium diethyl phosphite on 2-bromoacetophenone differs from that of the product of Arbuzov rearrangement (Fig. 1, Curve 5) by absence of a maximum in the region of 2850 A (enol form), and it is less characteristic. In this case insignificant change in absorption is observed in an alcoholic solution of sodium methoxide (Curve 6). A similar difference in spectrum is to be observed also for acetonylphosphonic ester and its homologs [4] prepared by the Arbuzov rearrangement on the one hand, and by the Michaelis-Becker reaction on the other.

Absorption spectra of alcoholic solutions of 2-oxocyclopentylphosphonic, 2-oxocyclohexylphosphonic, and 3-camphorylphosphonic esters prepared by Method B have no sharply marked maxima (Figures 3-5), as in other cases in which the compounds have been prepared by reaction of α-halo carbonyl compounds with sodium diethyl phosphite. Addition of sodium methoxide to their alcoholic solutions does not affect the character of their absorption appreciably.

It was considered to be interesting to compare the spectra of preparations of 2-oxocyclopentyl-, 2-oxocyclohexyl-, and 3-camphoryl-phosphonic esters synthesized by Methods A and B, but their preparation by Arbuzov rearrangement did not give satisfactory results. The spectrum of an alcoholic solution of diethyl 1-methyl-2-oxocyclohexylphosphonate prepared by Method A and incapable of enolization * shows greater absorption in the region of 2300 A (Fig. 4, Curve 3) than that of compounds prepared by Method B. In this case the absorption curve is smooth and, as would be expected, is unaffected by addition of sodium methoxide to the alcohol.

EXPERIMENTAL

Diethyl Phenacylphosphonate was prepared by two methods.

a) Preparation by the action of triethyl phosphite on 2-bromoacetophenone. 2-Bromoacetophenone (40 g) was melted and heated to 130°, and 34 g of triethyl phosphite was added dropwise; 17.5 g of ethyl bromide was distilled off. Vacuum fractionation gave two fractions: Fraction I, 5 g, b.p. 157-160° (1 mm) and Fraction II,

* As indicated in Table 2, it has 10% unsaturation according to the bromine titration.

(84%), b.p. 170-173° (2.5 mm), 39.5 g; n_D^{20} 1.5120; d_0^{20} 1.1650; found MR 66.01, calculated MR 64.89. The product has a golden color.

b) Preparation by the action of sodium diethyl phosphite on 2-bromoacetophenone. Reaction between 5 g of sodium and 30 g of diethyl hydrogen phosphite in ether gave sodium diethyl phosphite, to which an ethereal solution of 43 g of 2-bromoacetophenone was added. Toward the end of the addition the flask was heated in a water bath for one hour. After separation of sodium bromide and removal of ether, the residue was vacuum-distilled and gave Fraction I, 6 g, b.p. up to 163° (6 mm); Fraction II, 20 g. b.p. 163-167° (6 mm); and Fraction III, 16 g, b.p. 167-190° (6 mm). Redistillation of the fraction of b.p. 163-167° (6 mm) through a Widmer column gave a fraction of b.p. 165° (5 mm); n_D^{20} 1.4990; d_0^{20} 1.1615; found MR 64.89; calculated MR 64.79. Hydrolysis of the product with 1 : 1 aqueous hydrochloric acid in a sealed tube at 120° for eight hours gave a very small amount of phenacylphosphonic acid, m.p. 142-144°.

Diethyl α-Methylphenacylphosphonate was prepared by the action of 2-bromopropiophenone on triethyl phosphite. Triethyl phosphite (17.55 g) was added dropwise to 24 g 2-bromopropiophenone, b.p. 113-114° (3 mm) [16], heated to 160°. Toward the end of the reaction the bath temperature was 180-190°. Ethyl bromide distilled off as it was formed. Vacuum distillation gave 18.5 g (65%) of diethyl α-methylphenacylphosphonate, b.p. 156.5-158° (1.5 mm); n_D^{20} 1.5075; d_0^{20} 1.1328; found MR 71.00; calculated MR 69.51

Found %: P 11.60; 11.79. $C_{13}H_{19}O_4P$. Calculated %: P 11.47

Diethyl α,α-Dimethylphenacylphosphonate was prepared by the action of 2-bromo-2-methylpropiophenone on triethyl phosphite. Triethyl phosphite (15.7 g) was added dropwise to 21.5 g of 2-bromo-2-methylpropiophenone, b.p. 110-112° (3.5 mm) [17], heated to 140°. Toward the end of the reaction the bath temperature was 200°. The ethyl bromide formed was distilled off as it was produced (6.5 g). Vacuum distillation gave two fractions: Fraction I, 5 g, b.p. 62-70° (1.5 mm), and Fraction II, 20.5 g (75%), b.p. 137-138.5° (1 mm); n_D^{20} 1.4990; d_0^{20} 1.1052; found MR 75.53; calculated MR 74.13.

Found %: P 10.78; 10.83. $C_{14}H_{21}O_4P$. Calculated %: P 10.90

Diethyl 2-Oxocyclopentylphosphonate was prepared by the action of 2-chlorocyclopentanone on sodium diethyl phosphite. 2-Chlorocyclopentanone was prepared by Ketz's method [18] and had b.p. 74-76° (10 mm). Sodium diethyl phosphite was prepared in a ligroin medium (200 ml) from 6.4 g of sodium and 38.2 g of diethyl hydrogen phosphite. The solution of sodium diethyl phosphite was added gradually to a solution of 30 g of 2-chlorocyclopentanone in ligroin. With the addition of the first few drops a brown color appeared, the mixture became hot, and a fine precipitate of sodium chloride formed. The precipitate settled very slowly; it was filtered off and washed with ligroin. Ligroin was distilled off and the residue was vacuum-fractionated. A golden-colored substance came over at 110-121° (1.5 mm) and brownish-red substance remained. This residue gave 19.5 g (32%) of a slightly yellowish-green substance, b.p. 104-105° (1 mm); n_D^{20} 1.4560; d_0^{20} 1.1408; found MR 52.48; calculated MR 52.61.

Found %: P 13.72; 13.76. $C_9H_{17}O_4P$. Calculated %: P 14.07

Diethyl 1-Methyl-2-oxocyclohexylphosphonate. 2-Chloro-2-methylcyclohexanone was prepared by Warnhoff and Johnsons's method [19] and had b.p. 71-72° (14 mm) and n_D^{18} 1.4680.

a) By reaction of 2-chloro-2-methylcyclohexanone (24.7 g) with triethyl phosphite (28 g) (bath temperature at end of reaction 215°) the following fractions were obtained: Fraction I, b.p. 52-96° (1 mm) and Fraction II, 35 g, b.p. 112-114° (0.75 mm). Redistillation of the higher fraction gave diethyl 1-methyl-2-oxocyclohexylphosphonate, b.p. 118-120° (1 mm); n_D^{20} 1.4565, d_0^{20} 1.0860; found MR 62.19; calculated MR 61.73.

Found %: P 12.60. $C_{11}H_{21}O_4P$. Calculated % P 12.48.

b) 2-Chloro-2-methylcyclohexanone was treated with sodium diethyl phosphite. The latter was prepared in a ligroin medium from 4.7 g of sodium and 28.25 g of diethyl hydrogen phosphite, and the resulting solution was added gradually to 30 g of 2-chloro-2-methylcyclohexanone. The mixture became warm, and a precipitate of sodium chloride formed and was allowed to settle. The supernatant liquid was decanted, and the residue was washed with ligroin and filtered off on a No.4 glass filter (12 g). Ligroin was distilled off, and a clear yellowish viscous mass remained. Vacuum fractionation gave Fraction I, b.p. 65-98° (15 mm) and Fraction II,

b.p. 120-125° (1.5 mm). Redistillation of Fraction II gave 18.5 g (36.5%) of a yellowish substance, b. p. 119.5-121.5° (1 mm); n_D^{20} 1.4675; d_0^{20} 1.0902, found MR 63.26; calculated MR 61.73;

Found %: P 11.92; 12.20. $C_{11}H_{21}O_4P$. Calculated %: P 12.48

Diethyl 2-Oxocyclohexylphosphonate was synthesized by the action of sodium diethyl phosphite on 2-chlorocyclohexanone in ether [20]; it had b.p. 146-147° (8 mm); n_D^{20} 1.4595; d_0^{20} 1.1234; found MR 57.06; calculated MR 57.27.

An attempt to methylate the 2-oxocyclohexylphosphonic ester via its sodium or potassium derivative, which was treated with methyl iodide, did not give any positive results. Potassium and sodium reacted with the 2-oxocyclohexylphosphonic ester, but reaction of methyl iodide with the products gave only clear resins.

Preparation of 3-Camphorylphosphonate. Sodium diethyl phosphite was prepared from 4.6 g of sodium and 27.6 g of diethyl hydrogen phosphite in ligroin of b.p. 80-120°. The solution of sodium diethyl phosphite was added to a solution of 46.2 g of 3-bromocamphor in ligroin. The mixture became very warm, and sodium bromide was precipitated. Toward the end of the reaction the flask was heated in a water bath for 40 minutes. Sodium bromide was separated, ligroin was distilled off, and the residue was vacuum-fractioned: Fraction I, b.p. 70-117° (1.5 mm) (solidified) and Fraction II, b.p. 117-136° (1.5 mm). Redistillation of Fraction II gave 34 g (59%) of a product of b.p. 125-127° (1 mm) and 116-117° (0.5 mm); n_D^{20} 1 4600 d_0^{20} 1.0842; found MR 72.8; calculated MR 73.40.

Found %: P 10.81; 10.78 $C_{14}H_{26}O_4P$. Calculated %: P 10.75

Fractionation of the lower fractions gave 3-bromocamphor, m.p. 75-76°.

SUMMARY

1. With the object of studying their tautomerism, the following compounds were synthesized for the first time: diethyl α, α-dimethylphenacylphosphonate, diethyl 1-methyl-2-oxocyclohexylphosphonate, diethyl 2-oxocyclopentylphosphonate, and diethyl 3-camphorylphosphonate; their degrees of unsaturation were determined by the K. Meyer method of bromine titration. The constants of diethyl phenacylphosphonate prepared from triethyl phosphite differ from the constants of the diethyl phenacylphosphonate prepared by the Michaelis-Becker method.

2. The ultraviolet absorption spectra of the synthesized compounds were determined. The absorption spectra of phenacylphosphonic and α-methylphenacylphosphonic esters indicate the presence of enol forms and, in presence of sodium methoxide, the formation of enol anions. The spectra of phenacylphosphonic ester prepared via triethyl phosphite and of the same ester prepared by the Michaelis-Becker reaction differ from one another. The causes of this difference were elucidated.

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SOME PHOSPHORIC, PHOSPHOROUS, AND PHOSPHOROTHIONIC ESTERS OF ETHYLIDENE ETHERS OF GLYCEROL (2-METHYL-1,3-DIOXOLANE-4- METHANOL AND 2-METHYL-5-m-DIOXANOL)

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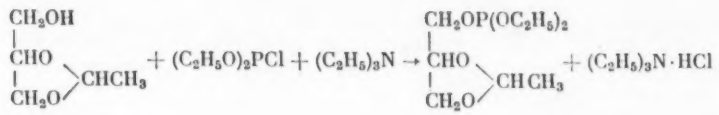
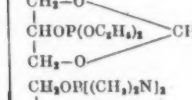
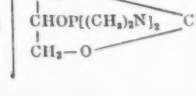
Phosphoric, phosphorous, and phosphorothionic esters of ethylidene ethers of glycerol, i.e., of the 5- and 6-membered cyclic compounds 2-methyl-1,3-dioxolane-4-methanol and 2-methyl-5-m-dioxanol, have not beeen described in the literature. The study of these compounds is of some interest both from the point of view of their chemical properties and also from the point of view of their physiological properties, because compounds of the type 2-alkyl-1,3-dioxolane-4-methanol have an insectifugal action [1]. We studied mono- and bis-(2-methyl-1,3-dioxolan-4-yl) methyl and -2-methyl-5-m-dioxanyl esters of phosphoric, phosphorous, and phosphorothionic acids and related esters of, e. g., dimethylphosphoramidous and dimethylphosphoramidic acids, and we also began a study of the Arbuzov rearrangement of such compounds.

Diethyl (2-methyl-1,3-dioxolan-4-yl) methyl phosphite and diethyl 2-methyl-5-m-dioxanyl phosphite were prepared directly by the reactions of 2-methyl-1,3-dioxolane-4-methanol and 2-methyl-5-m-dioxanol with diethyl phosphorochloridite in presence of triethylamine for the binding of hydrogen chloride formed in the reaction:

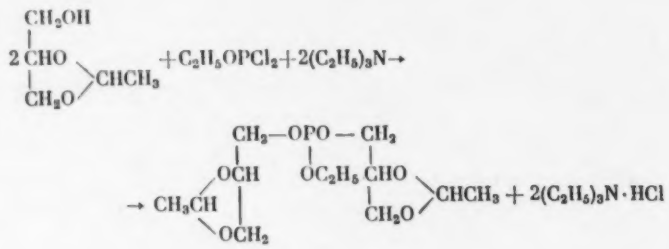


the equation for reaction with 2-methyl-5-m-dioxanol being analogous. (2-Methyl-1,3-dioxolan-4-yl)methyl and 2-methyl-5-m-dioxanyl tetramethylphosphorodiamidites were prepared by the action of the alcohols on tetramethylphosphorodiamidous chloride in presence of triethylamine. Constants of these esters are given in Table 1.

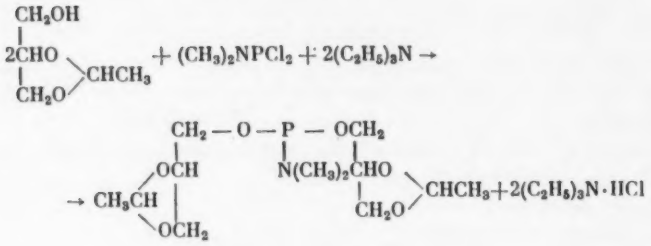
TABLE 1.

No.	Formula of ester	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	*MR* Found	*MR* Calculated	Yield (%)
1		79 (0.5)	1.4390	1.0764	58.15	57.94	70
2		97 (2)	1.4490	1.1017	57.91	57.94	63.8
3		78—79 (2)	1.4650	1.0435	62.52	62.30	67.8
4		85 (2)	1.4708	1.0522	62.66	62.30	68

Bis (2-methyl-1,3-dioxolan-4-ylmethyl) and bis (2-methyl-5-m-dioxanyl) esters were prepared by reaction of the same alcohols with Menshutkin's acid chloride (ethyl phosphorodichloridite) and with dimethylphosphoramidous dichloride in an ether medium in presence of triethylamine:



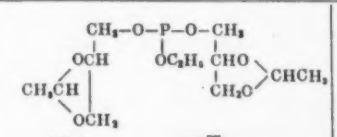
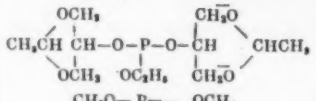
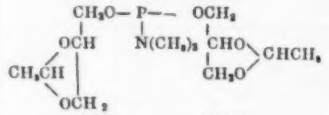
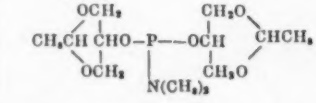
(1)



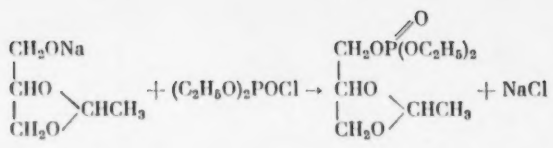
(2)

The constants of the esters obtained are given in Table 2. They are fairly viscous odorless liquids; bis (2-methyl-5-m-dioxanyl) dimethylphosphoramidite solidified after fractional distillation.

TABLE 2

No.	Formula of ester	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	MR Found	MR Calculated	Yield (%)
1		125 (0.5)	1.4550	1.1533	72.99	72.84	60.8
2		137—139 (1)	1.4688	1.1916	72.99	72.84	42
3		132 (1)	1.4644	1.1340	75.24	75.04	68
4		145 (1) Crystalline product, m.p. 52-53°					53

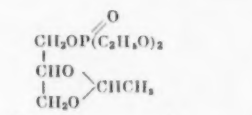
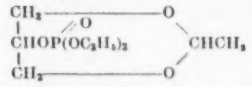
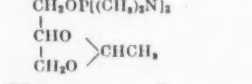
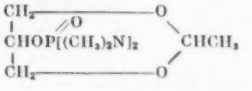
Diethyl (2-methyl-1,3-dioxolan-4-yl) methyl phosphate and diethyl 2-methyl-5-m-dioxanyl phosphate were prepared by reaction of the sodium derivatives of the same alcohols with diethyl phosphorochloridite in dry benzene as solvent:



the equation for reaction with 2-methyl-5-m-dioxanol being analogous.

Constants of the esters obtained are given in Table 3(No. 1 and 2). (2-Methyl-1,3-dioxolan-4-yl)methyl and 2-methyl-5-m-dioxanyl tetramethylphosphorodiamidates were prepared from the sodium derivatives of the alcohols by reaction with tetramethylphosphorodiamidic chloride in dry gasoline (b.p. 80-125°) as solvent. The reaction is analogous to that described above. The products are listed in Table 3 (No. 3 and 4).

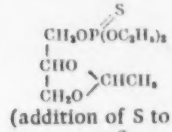
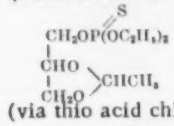
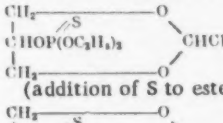
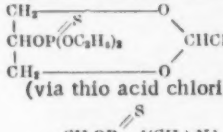
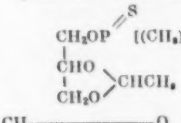
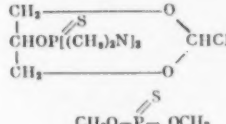
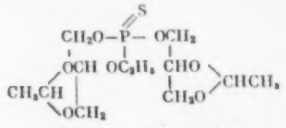
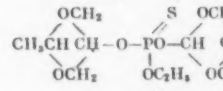
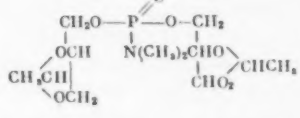
TABLE 3

No.	Formula of ester	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	MR Found	MR Calculated	Yield (%)
1		119 (4)	1.4318	1.1603	56.75	56.79	53.1
2		113 (1)	1.4380	1.1757	56.71	56.79	44.5
3		113 (1)	1.4550	1.1241	60.82	61.18	63.5
4		104—105 (2)	1.4600	1.1366	60.81	61.18	55.0

The thio analogs of these phosphoric and phosphorodiamidic esters were also of interest both from the point of view of their physiological activity and also from the point of view of the study of the chemical properties of the corresponding phosphorous esters. 0,0-Diethyl 0-(2-methyl-1,3-dioxolan-4-yl)methyl phosphorothioate and 0,0-diethyl 0-(2-methyl-5-m-dioxanyl) phosphorothioate were prepared by two methods: 1) addition of sulfur to the corresponding phosphorous esters, and 2) reaction of the sodium derivatives of 2-methyl-1,3-dioxolane-4-methanol and 2-methyl-5-m-dioxanol with 0,0-diethyl phosphorochloridothioate. Constants of esters prepared in the two ways are listed in Table 4 (No. 1, 1a, 2, 2a). The phosphorodiamidothionic esters were prepared by addition of sulfur to the corresponding phosphorodiamidothionous esters and are also listed in Table 4 (No. 3 and 4). By addition of sulfur to the phosphorous and phosphoroamidous esters containing two cyclic radicals we prepared 0-ethyl 0,0-bis (2-methyl-1,3 -dioxolan-4-ylmethyl) phosphorothioate and 0-ethyl 0,0-bis- (2-methyl-5-m-dioxanyl) phosphorothioate (Table 4, No. 5 and 6) and also an analogous ester of dimethylphosphoroamidothionic acid (Table 4, No. 7).

As can be seen from Table 4, for all these derivatives of phosphorothionic acid the calculated values of molecular refraction exceed the experimentally determined values by an approximately constant amount, 0.5, which enables us to make a correction in the atomic refraction of sulfur in esters of this sort.

TABLE 4

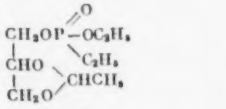
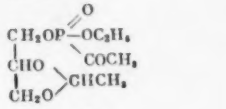
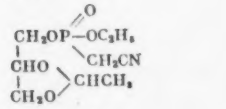
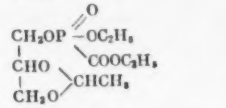
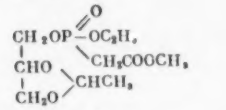
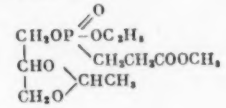
No.	Formula of ester	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	MR Found*	MR Calculated	Difference	Yield (%)
1	 (addition of S to ester)	113–114 (1)	1.4636	1.1575	64.35	64.84	0.49	79.4
1a	 (via thio acid chloride)	111 (0.5)	1.4641	1.1583	64.35	64.84	0.49	55.5
2	 (addition of S to ester)	113–114 (1)	1.4685	1.1651	64.44	64.84	0.40	65.0
2a	 (via thio acid chloride)	119 (2,5)	1.4731	1.1781	64.34	64.84	0.50	50.0
3		118–118.5(0.2)	1.4907	1.1317	68.55	69.14	0.59	50.0
4		120 (1)	1.4980	1.1446	68.63	69.14	0.51	62.5
5		138 (0.5)	1.4740	1.2133	79.22	79.79	0.57	50.0
6		155–157 (0.5)	1.4820	Very viscous liquid				
7		153 (0.5)	1.4848	1.1997	81.48	81.98	0.56	30.0

* Atomic refractions: P = 4.27; S = 9.7; N = 2.74 [2].

Arbuzov rearrangement of the esters obtained was studied for the case of diethyl (2-methyl-1,3-dioxolan-4-yl)methyl phosphite in its reaction with various halogen compounds. The isomerization reaction was carried out with ethyl bromide, and rearrangement reactions were carried out with acetyl chloride, chloroacetonitrile, ethyl chloroformate, methyl chloroacetate, and methyl 3-chloropropionate. In this way six new phosphonic esters were obtained. Constants of these esters are given in Table 5.

Tests were carried out on the insecticidal activities of the esters for the corn weevil. No positive results were obtained. Thus, a 1% concentration of diethyl (2-methyl-1,3-dioxolan-4-yl)methyl phosphate was required to produce 100% mortality in two days. With respect to insecticidal activity as a contact poison, the

TABLE 5

No.	Formula of ester	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	MR Found	MR Calculated	Yield (%)
1		163—164 (2)	1.4400	1.1315	55.42	55.18	66
2		131 (2)	1.4470	1.1962	56.29	55.16	50
3		156 (0.5)	1.4536	1.2114	55.62	54.96	50
4		132.5—133 (1)	1.4440	1.1993	62.46	61.42	51
5		136—137 (0.5)	1.4506	1.2248	61.94	61.42	68
6		150—151 (3)	1.4510	1.2012	65.23	66.04	30

amido esters were still less toxic; thus, a 1% concentration of (2-methyl-1,3-dioxolan-4-yl) methyl tetramethylphosphorodiamidate was required to produce 36% mortality in ten days. 0,0-Diethyl O-(2-methyl-1,3-dioxolan-4-yl) methyl phosphorothioate was found to be almost nontoxic to the corn weevil: a 1% concentration gave 2% mortality in six days.

EXPERIMENTAL

Preparation of (2-Methyl-1,3-dioxolan-4-yl)methyl and 2-Methyl-5-m-dioxanyl Esters of Phosphorous and Tetramethylphosphorodiamidous Acids

1. Synthesis of Diethyl (2-Methyl-1,3-dioxolan-4-yl) methyl Phosphite. A mixture of 11.8 g of 2-methyl-1,3-dioxolane-4-methanol [3][b.p. 82-90° (10 mm) n_D^{20} 1.4390], 10.1 g of triethylamine, and 200 ml of dry ether was prepared in a three-necked flask fitted with stirrer, reflux condenser, and dropping funnel. With cooling and vigorous stirring 15.6 g of diethyl phosphorochloridite was added dropwise. Stirring was then continued without cooling for 4-5 hours. The precipitate of triethylamine hydrochloride was filtered off, ether was distilled off, and vacuum fractionation of the residue from an Arbuzov flask gave 20 g of a substance of b.p. 82-95° (2 mm). This substance was refractionated through a Widmer column and gave 16.5 g (70%) of diethyl (2-methyl-1,3-dioxolan-4-yl)methyl phosphite, b.p. 79° (0.5 mm); n_D^{20} 1.4390; d_4^{20} 1.0764; found MR 58.15; calculated $C_9H_{19}O_5P$ MR 57.94.

Found %: P 13.12; 12.90 $C_9H_{19}O_5P$. Calculated %: P 13.02

2. Synthesis of Diethyl 2-Methyl-5-m-dioxanyl Phosphite. The procedure was similar to that of the preceding experiment. Reaction was between 11.8 g of 2-methyl-5-m-dioxanol [3] [b.p. 68° (10 mm); n_D^{17} 1.4510], 11 g of triethylamine, and 15.6 g of diethyl phosphorochloridite. The ester obtained, amounting to 15.2 g (63.8%) had the following constants: b.p. 97.5° (2 mm); d_4^{20} 1.1017; n_D^{20} 1.4490; found MR 57.91; calculated for $C_9H_{19}O_5P$ MR 57.94.

Found %: P 13.23; 13.04 $C_9H_{19}O_5P$. Calculated % P 13.02

3. Synthesis of (2-Methyl-1,3-dioxolan-4-yl)methyl Tetramethylphosphorodiamidite. The reactants were 2-methyl-1,3-dioxolane-4-methanol (11.8 g), triethylamine (10.1 g), and tetramethylphosphorodiamidous chloride (15.5 g). The procedure was analogous to that described above, but the second fractionation was carried out from an Arbuzov flask. The resulting (2-methyl-1,3-dioxolan-4-yl) methyl tetramethylphosphorodiamidate, amounting to 14.2 g (67.8%), had the following constants: b.p. 78-79° (2 mm); n_D^{20} 1.4650; d_4^{20} 1.0435; found MR 65.52; calculated for $C_9H_{21}O_3N_2P$ MR 62.30.

Found %: P 13.39; 13.27 $C_9H_{21}O_3N_2P$. Calculated %: P 13.13

4. Synthesis of 2-Methyl-5-m-dioxanyl Tetramethylphosphorodiamidite. An analogous procedure was used. The reactants were 2-methyl-5-m-dioxanol (11.8 g), triethylamine (10.1 g), and tetramethylphosphorodiamidous chloride (15.5 g). The resulting ester, amounting to 15.5 g (65%), had the following constants: b.p. 85° (2 mm); d_4^{20} 1.0522; n_D^{20} 1.4708; found MR 62.66; calculated for $C_9H_{21}O_3N_2P$ MR 62.30.

Found %: P 13.42, 13.42 $C_9H_{21}O_3N_2P$. Calculated % P 13.13

Preparation of Bis (2-methyl-1,3-dioxolan-4-ylmethyl) and Bis (2-methyl-5-m-dioxanyl) Esters of Phosphorous and Dimethylphosphoramidous Acids.

1. Synthesis of Ethyl Bis (2-methyl-1,3-dioxolan-4-ylmethyl) Phosphite. The reactants taken were 2-methyl-1,3-dioxolane-4-methanol (20.6 g), triethylamine (17.65 g), and Menshutkin's acid chloride (12.85 g). The ester obtained (18.5 g, i.e., 60.8%) had b.p. 125° (0.5 mm); n_D^{20} 1.4555; d_4^{20} 1.1533; found MR 72.99; calculated for $C_{12}H_{23}O_7P$ MR 72.84.

Found %: P 10.14, $C_{12}H_{23}O_7P$. Calculated %: P 10.00

2. Synthesis of Ethyl Bis (2-methyl-5-m-dioxanyl) Phosphite. The reactants were 2-methyl-5-m-dioxanol (11.8 g), triethylamine (10.1 g), and Menshutkin's acid chloride (7.35 g). The product (6.5 g, i. e., 42%) had b.p. 137-139° (1 mm); n_D^{20} 1.4688; d_4^{20} 1.1916; found MR 72.42; calculated for $C_{12}H_{23}O_7P$ MR 72.84.

Found %: P 10.05; 10.21 $C_{12}H_{23}O_7P$. Calculated %: P 10.00

3. Synthesis of Bis (2-methyl-1,3-dioxolan-4-ylmethyl) Dimethylphosphoramidite. The reactants were 2-methyl-1,3-dioxolane-4-methanol (23.6 g), triethylamine (20.2 g), and dimethylphosphoramidous dichloride (14.6 g). The resulting bis (2-methyl-1,3-dioxolan-4-ylmethyl) dimethylphosphoramidite (21 g, i.e., 68%) had b.p. 132° (1 mm); n_D^{20} 1.4644; d_4^{20} 1.1340; found MR 75.24; calculated for $C_{12}H_{24}O_6NP$ MR 75.04.

Found %: P 10.02; 10.00 $C_{12}H_{24}O_6NP$. Calculated %: P 10.03

4. Synthesis of Bis (2-methyl-5-m-dioxanyl) Dimethylphosphoramidite. The reactants were 2-methyl-5-m-dioxanol (11.8 g), triethylamine (10.1 g), and dimethylphosphoramidous dichloride (7.3 g). The product (6 g, i.e., 39%) had b.p. 145° (1 mm) and m.p. 52-53°.

Found %: P 10.16; 10.12 $C_{12}H_{24}O_6NP$. Calculated %: P 10.03

Preparation of (2-Methyl-1,3-dioxolan-4-yl)methyl and 2-Methyl-5-m-dioxanyl Esters of Phosphoric and Tetramethylphosphorodiamidic Acids.

1. Synthesis of Diethyl (2-Methyl-1,3-dioxolan-4-yl)methyl Phosphate. Dry gasoline (100 ml) and sodium (4 g; an excess) were introduced into a three-necked flask fitted with stirrer, reflux condenser, and dropping funnel, and 11.8 g of 2-methyl-1,3-dioxolane-4-methanol was added. The sodium reacted almost quantitatively with the alcohol. The excess of sodium (1.7 g) was removed after the reaction mixture had been

heated at 85° for one hour, and 17.2 g of diethyl phosphorochloridate was then added. The flask was then heated in a water bath for a further three hours. The precipitate of sodium chloride was centrifuged off, and the residue, after removal of gasoline, was vacuum-fractionated from an Arbuzov flask. A fraction (15.3 g) of b.p. 110-123° (1 mm) was collected, and this was refractionated from a flask fitted with a Widmer column. The resulting diethyl (2-methyl-1,3-dioxolan-4-yl)methyl phosphate (13.5 g, i.e., 53%) had b.p. 119° (4 mm); n_D^{20} 1.4318; d_4^{20} 1.1603; found MR 56.75; calculated for $C_9H_{19}O_6P$ MR 56.79.

Found %: P 12.52; 12.62 $C_9H_{19}O_6P$. Calculated %: P 12.20

The following results were obtained in tests on insecticidal activity toward the corn weevil: 0.05% concentration – 28% mortality in seven days; 0.5% concentration – 80% mortality in seven days; 1% concentration – 100% mortality in two days.

In all the succeeding experiments the synthesis of phosphoric esters was carried out similarly.

2. Synthesis of Diethyl 2-Methyl-5-m-dioxanyl Phosphate. The reactants were 2-methyl-5-m-dioxanol (11.8 g), sodium (4 g; an excess), and diethyl phosphorochloridate (17.2 g). The resulting ester (11.3 g, i.e., 44.5%) had b.p. 113° (1 mm); n_D^{20} 1.4380; d_4^{20} 1.1757; found MR 56.71; calculated for $C_9H_{19}O_6P$ MR 56.79.

Found %: P 12.60; 12.52 $C_9H_{19}O_6P$. Calculated %: P 12.20

Tests on insecticidal activity toward the corn weevil gave: 0.05% concentration – 32% mortality in seven days; 0.5% concentration – 46% mortality in seven days; 1% concentration – 100% mortality in three days.

3. Synthesis of (2-Methyl-1,3-dioxolan-4-yl)methyl Tetramethylphosphorodiamidate. The reactants were 2-methyl-1,3-dioxolane-4-methanol (23.6 g), sodium (7 g; an excess), and tetramethylphosphorodiamidic chloride (34 g). The resulting ester (32 g, i.e., 63.5%) had b.p. 113° (1 mm); d_4^{20} 1.1241; n_D^{20} 1.4550; found MR 60.82; calculated for $C_9H_{21}O_4N_2P$ MR 61.18.

Found %: P 12.48; 12.45 $C_9H_{21}O_4N_2P$. Calculated %: P 12.30

Tests on insecticidal activity toward the corn weevil gave: 1% concentration – 36% mortality in ten days.

4. Synthesis of 2-Methyl-5-m-dioxanyl Tetramethylphosphorodiamidate. The reactants were 2-methyl-5-m-dioxanol (11.8 g), sodium (4 g), and tetramethylphosphorodiamidic chloride (17 g). The resulting ester (13.8 g, i.e., 55%) had b.p. 104-105°; d_4^{20} 1.1366; n_D^{20} 1.4600; found MR 60.81; calculated for $C_9H_{21}O_4N_2P$ MR 61.18.

Found %: P 12.25; 12.20 $C_9H_{21}O_4N_2P$. Calculated %: P 12.30

Preparation of (2-Methyl-1,3-dioxolan-4-yl)methyl and 2-Methyl-5-m-dioxanyl Esters of Phosphorothionic, Dimethylphosphoramidothionic, and Tetramethylphosphorodiamidothionic Acids

1. Synthesis of 0,0-Diethyl 0-(2-Methyl-1,3-dioxolan-4-yl)methyl Phosphorothioate. a) Addition of Sulfur to the ester. Sulfur (1 g) was added in small portions to 7 g of diethyl (2-methyl-1,3-dioxolan 4-yl) methyl phosphite. The temperature rose to 95°, and the mixture was then heated to 150°. Vacuum fractionation from an Arbuzov flask gave 6.45 g (79.4%) of the phosphorothioic ester, b.p. 113-114° (1 mm); n_D^{20} 1.4636; d_4^{20} 1.1575; found MR 64.35; calculated for $C_9H_{19}O_5SP$ MR 64.84.

Found %: P 11.52; 11.42 $C_9H_{19}O_5SP$. Calculated %: P 11.48

b) Synthesis via the acid chloride. The synthesis was analogous to that of diethyl (2-methyl-1,3-dioxolan-4-yl)methyl phosphate. The reactants were 2-methyl-1,3-dioxolane-4-methanol (5.9 g), sodium (2 g), and 0,0-diethyl phosphorochloridothioate (9.4 g). The ester (7.5 g, i.e., 55.5%) had b.p. 111° (0.5 mm); n_D^{20} 1.4611; d_4^{20} 1.1583; found MR 64.35; calculated for $C_9H_{19}O_5SP$ MR 64.84.

Found %: P 11.44; 11.47 $C_9H_{19}O_5SP$. Calculated %: P 11.48

2. Synthesis of 0,0-Diethyl 0-(2-Methyl-5-m-dioxanyl) Phosphorothioate. a) Addition of sulfur to the ester. Sulfur (0.7 g) was added to 5 g of diethyl 2-methyl-5-m-dioxanyl phosphite. The temperature of the mixture rose to 75°. Two fractional distillations gave 3.5 g (65%) of the addition product, b.p. 113-114° (1 mm); n_D^{20} 1.4685; d_4^{20} 1.1651; found MR 64.44; calculated for $C_9H_{19}O_5SP$ MR 64.84.

Found %: P 11.63; 11.67 $C_9H_{19}O_5SP$. Calculated %: P 11.48

b) Via the acid chloride. The synthesis was similar to that of diethyl 2-methyl-5-m-dioxanyl phosphate. The reactants were 2-methyl-5-m-dioxanol (10 g), sodium (4 g), and 0,0-diethyl phosphorochloridothioate (16 g). The ester (11.3 g, i.e., 50%) had b.p. 119° (2.5 mm); n_D^{20} 1.4731; d_4^{20} 1.1781; found MR 64.34; calculated for $C_9H_{19}O_5SP$ MR 64.84.

Found %: P 11.77 $C_9H_{19}O_5SP$. Calculated %: P 11.48

Tests on insecticidal activity toward the corn weevil: at 1% concentration – 2% mortality in six days.

3. Synthesis of 0-(2-Methyl-1,3-dioxolan-4-yl)methyl Tetramethylphosphorodiamidothioate. Addition of 2 g of sulfur to 10 g of (2-methyl-1,3-dioxolan-4-yl)methyl tetramethylphosphorodiamidite gave the corresponding phosphorothioic derivative (5.5 g, i.e., 50%), b.p. 118-118.5° (0.2 mm); n_D^{20} 1.4907; d_4^{20} 1.1317; found MR 68.55; calculated for $C_9H_{21}O_3PSN_2$ MR 69.14.

Found %: P 11.77; 11.82 $C_9H_{21}O_3PSN_2$. Calculated %: P 11.57

4. Synthesis of 0-(2-Methyl-5-m-dioxanyl) Tetramethylphosphorodiamidothioate. This ester was synthesized by addition of sulfur to the corresponding phosphorous compound. The reactants were 2-methyl-5-m-dioxanyl tetramethylphosphorodiamidite (5 g) and sulfur (0.72 g). Fractionation gave 3.5 g (62%) of a product having b.p. 120° (1 mm); n_D^{20} 1.4980; d_4^{20} 1.1446; found MR 68.63; calculated for $C_9H_{21}O_3PSN_2$ MR 69.14.

5. Synthesis of 0-Ethyl 0,0-Bis (2-methyl-1,3-dioxolan-4-ylmethyl) Phosphorothioate. Reaction was between 10.5 g of ethyl bis (2-methyl-1,3-dioxolan-4-ylmethyl) phosphite and 1 g of sulfur. The resulting ester (5.5 g, i.e., 50%) had b.p. 138° (0.5 mm); d_4^{20} 1.2133; n_D^{20} 1.4740; found MR 79.22; calculated for $C_{12}H_{23}O_7PS$ MR 79.79.

Found %: P 9.07; 9.04 $C_{12}H_{23}O_7PS$. Calculated %: P 9.07

6. Synthesis of 0-Ethyl 0,0-Bis (2-methyl-5-m-dioxanyl) Phosphorothioate. The reactants were ethyl bis (2-methyl-5-m-dioxanyl) phosphite (5 g) and sulfur (0.5 g). The resulting ester had b.p. 155-157° (0.5 mm) and n_D^{20} 1.4820, but the density was not determined because of the very high viscosity of the product.

Found %: P 9.20; 9.21 $C_{12}H_{23}O_7PS$. Calculated %: P 9.07

7. Synthesis of 0,0-Bis (2-methyl-1,3-dioxolan-4-ylmethyl) Dimethylphosphoramidothioate. The reactants were bis (2-methyl-1,3-dioxolan-4-ylmethyl) dimethylphosphoramidite (8 g) and sulfur (0.9 g). The corresponding thio ester (2.7 g, i.e., 30%) had b.p. 153° (0.5 mm); n_D^{20} 1.4848; d_4^{20} 1.1997; found MR 81.48; calculated for $C_{12}H_{24}O_6NPS$ MR 81.98.

Found %: P 9.09; 9.05 $C_{12}H_{24}O_6NPS$. Calculated %: P 9.09

Action of Halogen Compounds on Diethyl (2-Methyl-1,3-dioxolan-4-yl)methyl Phosphite.

1. Action of Ethyl Bromide on Diethyl (2-Methyl-1,3-dioxolan-4-yl)methyl Phosphite. The isomerization of diethyl (2-methyl-1,3-dioxolan-4-yl)methyl phosphite was carried out in a sealed tube at 120-130° for eight hours. Reaction was between 5 g of ester and 3 g of ethyl bromide. The product (3.3 g, i.e., 66%) was ethyl (2-methyl-1,3-dioxolan-4-yl)methyl ethylphosphonate, b.p. 163-164° (2 mm); n_D^{20} 1.4400; d_4^{20} 1.1315; MR 55.42; calculated for $C_9H_{19}O_5P$ MR 55.18.

Found %: P 13.24; 13.10 $C_9H_{19}O_5P$. Calculated %: P 13.02

2. Action of Acetyl Chloride on Diethyl (2-Methyl-1,3-dioxolan-4-yl)methyl Phosphite. Acetyl chloride (2.6 g) was slowly dropped into 8 g diethyl (2-methyl-1,3-dioxolan-4-yl)methyl phosphite contained in a three-necked flask fitted with reflux condenser, thermometer, and dropping funnel. The temperature rose to 60° and throughout the reaction ethyl chloride separated. Vacuum fractionation of the product from an Arbuzov flask gave 4.2 g (50%) of ethyl (2-methyl-1,3-dioxolan-4-yl)methyl acetylphosphonate, b.p. 131° (2 mm); n_D^{20} 1.4470; d_4^{20} 1.1962; found MR 55.16; calculated for $C_9H_{17}O_6P$ MR 56.29.

Found %: P 12.37; 12.34 $C_9H_{17}O_6P$. Calculated %: P 12.30

4. Action of Ethyl Chloroformate on Diethyl (2- Methyl-1,3-dioxolan-4-yl)methyl Phosphite. Reaction was between 10 g of diethyl (2-methyl-1,3-dioxolan-4-yl)methyl phosphite and 4.5 g of ethyl chloroformate. The reaction temperature rose to 94°. Fractionation gave 6 g (51%) of ethyl (2-methyl-1,3-dioxolan-4-yl) methyl ethoxycarbonylphosphonate, b.p. 132.5-133° (1 mm); n_D^{20} 1.4440; d_4^{20} 1.1993; found MR 62.46; calculated for $C_{10}H_{19}O_7P$ MR 61.42.

Found %: P 10.94; 10.86 $C_{10}H_{19}O_7P$. Calculated %: P 11.00

5. Action of Methyl Chloroacetate on Diethyl (2-Methyl-1,3-dioxolan-4-yl)methyl Phosphite. Reaction was between 10 g of diethyl (2-methyl-1,3-dioxolan-4-yl)methyl phosphite and 4.5 g of methyl chloroacetate. The resulting ethyl (2-methyl-1,3-dioxolan-4-yl)methyl (methoxycarbonyl)methylphosphonate (8 g. i.e., 68%) had b.p. 137° (0.5 mm); n_D^{20} 1.4506; d_4^{20} 1.2248; found MR 61.94; calculated for $C_{10}H_{19}O_7P$ MR 60.85.

Found %: P 10.81; 10.85 $C_{10}H_{19}O_7P$. Calculated %: P 11.00

6. Action of Methyl 3-Bromopropionate on Diethyl (2-Methyl-1,3-dioxolan-4-yl)methyl Phosphite. Reaction was between 11 g of diethyl (2-methyl-1,3-dioxolan-4-yl)methyl phosphite and 4.5 g of methyl 3-bromopropionate. The resulting ester (3.9 g, i.e., 30%) had b.p. 150-151° (3 mm); n_D^{20} 1.4510; d_4^{20} 1.2012; found MR 65.23; calculated for $C_{11}H_{21}O_7P$ MR 66.04.

Found %: P 10.40; 10.77 $C_{11}H_{12}O_7P$. Calculated %: 10.65

SUMMARY

1. Nineteen new phosphorous, phosphoric and phosphorothionic esters and N-substituted phosphoramidous, phosphorodiamidous, phosphoramidic, phosphorodiamidic, phosphoramidothionic, and phosphorodiamidothionic esters of ethylidene ethers of glycerol (2-methyl-1,3-dioxolane-4-methanol and 2-methyl-5-m-dioxanol) were synthesized and studied.

2. The Arbuzov rearrangement of diethyl (2-methyl-1,3-dioxolan-4-yl)methyl phosphite was studied. Six new (2-methyl-1,3-dioxolan-4-yl)methyl phosphonates were prepared.

3. Some of the esters obtained were tested for insecticidal activity.

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PREPARATION OF POLYORGANOBOROSILOXANES BY HETEROFUNCTIONAL CONDENSATION

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Polyorganometallosiloxanes form a new class of polymers in which the molecular chain is made up of silicon, oxygen, and metal atoms. This class of compounds occupies a position intermediate between organosilicon polymers and silicates. As we have shown previously [1], by the action of metals or metal oxides on hydroxyl-containing organosilicon compounds, compounds of this new class are formed in accordance with the equation:

$$6HOR_2SiOSiR_2OH + 2Al \rightarrow 2\,[HOR_2SiOSiR_2O]_3\,Al + 3H_2.$$

Later, by means of an exchange reaction, we obtained the aluminum derivative of triethylsilanol [2]:

$$3\,(C_2H_5)_3SiONa + AlCl_3 \rightarrow [(C_2H_5)_3\,SiO]_3\,Al + 3NaCl.$$

A borosilicon ester has been prepared by the action of a boron trihalide on the sodium derivative of triethylsilanol [3]:

$$3\,(C_2H_5)_3SiONa + BBr_3 \rightarrow [(C_2H_5)_3\,SiO]_3\,B + 3NaBr.$$

Henglein and coworkers have investigated the synthesis of polyborosilicon esters [4].

In the present work we investigated the reaction of alkyl- and aryl-acetoxysilanes with tributyl borate and alkyl- and aryl-ethoxysilanes and alkyl- and aryl-butoxysilanes with boron triacetate. It was found that, when these compounds were heated together, condensation occurred with formation of polyorganoborosiloxanes, butyl or ethyl acetate being eliminated. Investigation of the condensation of alkyl- and aryl-acetoxysilanes with tributyl borate showed that, during the heating, the viscosity of the condensation product increased in accordance with the amount of butyl acetate eliminated. For example, in the condensation of diacetoxydimethylsilane with tributyl borate (Fig. 1), the acetyl content fell sharply in the first 90 minutes of the heating and at the same time much butyl acetate, attaining up to 70% of the theoretical amount, was eliminated. There was a simultaneous rise in the viscosity of the reaction product. Further heating led to insignificant elimination of butyl acetate and change in viscosity.

The experimental results showed that with change from the methyl radical to phenyl, i.e., in the condensation of diacetoxymethylphenylsilane with tributyl borate, the general picture was not changed: in this case also (Fig. 2) according to the amount of butyl acetate eliminated reaction proceeded to the extent of 75%, but the viscosity of the product rose more sharply, the average molecular weight of the polymer being higher for a given extent of condensation. These results show that, when alkyl- and aryl-acetoxysilanes are heated with tributyl borate, stepwise condensation occurs with formation of polyorganoborosiloxanes:

$$R_2Si(OCOCH_3)_2 + B(OC_4H_9)_3 \rightarrow CH_3COOSiR_2OB(OC_4H_9)_2 + CH_3COOC_4H_9 \quad \text{(a)}$$

$$CH_3COOSiR_2OB(OC_4H_9)_2 + R_2Si(OCOCH_3)_2 \rightarrow$$

$$\rightarrow CH_3COOSiR_2OBO - SiR_2OCOCH_3 + CH_3COOC_4H_9 \quad \text{(b)}$$

$$\quad\quad\quad

Reaction continued by condensation of these products among themselves and with monomers with formation of complex polymeric molecules. With increase in the viscosity of the polymer the stepwise condensation became slower and did not go to completion. When equimolecular amounts of dibutoxymethylphenylsilane and boron triacetate were heated together, condensation again occurred with increase in viscosity, change in acetyl content, and elimination of butyl acetate (Fig. 3). The experimental results on reaction between equimolecular amounts of dibutoxydimethylsilane and boron triacetate (Fig. 4) showed that stepwise condensation again ocurred with elimination of butyl acetate :

$$(CH_3)_2Si(OC_4H_9)_2 + B(OCOCH_3)_3 \rightarrow (CH_3)_2Si\underset{\displaystyle OC_4H_9}{\underset{|}{O}}B(OCOCH_3)_2 + C_4H_9OCOCH_3 \qquad (a)$$

$$(CH_3)_2SiOB(OCOCH_3)_2 + (CH_3)_2Si(OC_4H_9)_2 \rightarrow$$
$$\rightarrow C_4H_9OSi(CH_3)_2OBOSi(CH_3)_2OC_4H_9 + CH_3COOC_4H_9 \qquad (b)$$

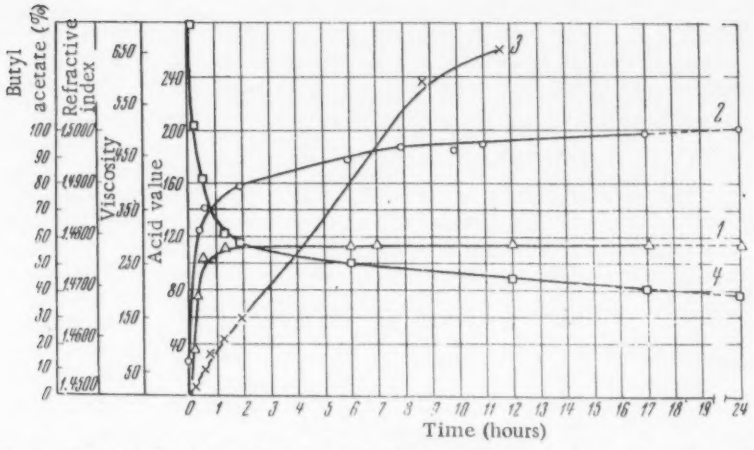

Fig. 3. Reaction between dibutoxymethylphenylsilane and boron triacetate: 1) amount of butyl acetate eliminated (%); 2) refractive index; 3) viscosity (centipoise); 4) acid value.

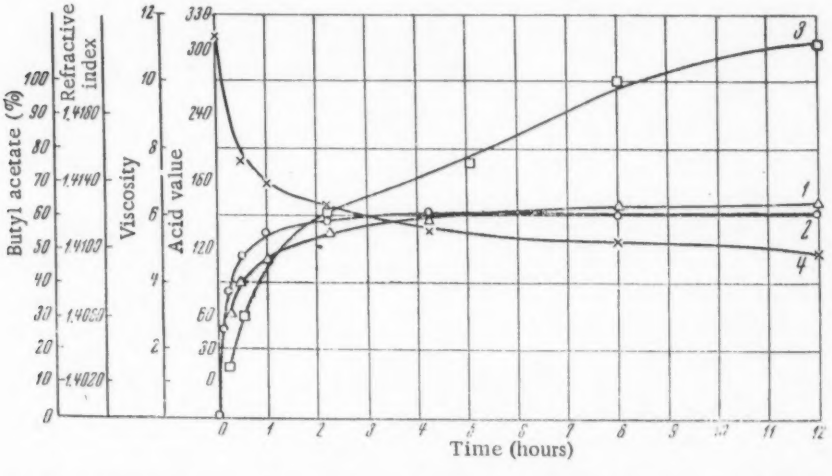

Fig. 4. Reaction between dibutoxydimethylsilane and boron triacetate: 1) refractive index; 2) amount of butyl acetate eliminated (%); 3) viscosity (centipoise); 4) acid value.

This reaction is considerably more rapid and complete when butoxyl is replaced by ethoxyl in the alkyl- or aryl-alkoxysilane. Thus, reaction between diethoxymethylphenylsilane and boron triacetate proceeds to the extent of 86% (Fig. 5), whereas reaction between dibutoxymethylphenylsilane and boron triacetate proceeds only to the extent of 57.0%. All the resulting polymers are light-brown viscous products, readily soluble in alcohol, acetone, dioxane, and toluene.

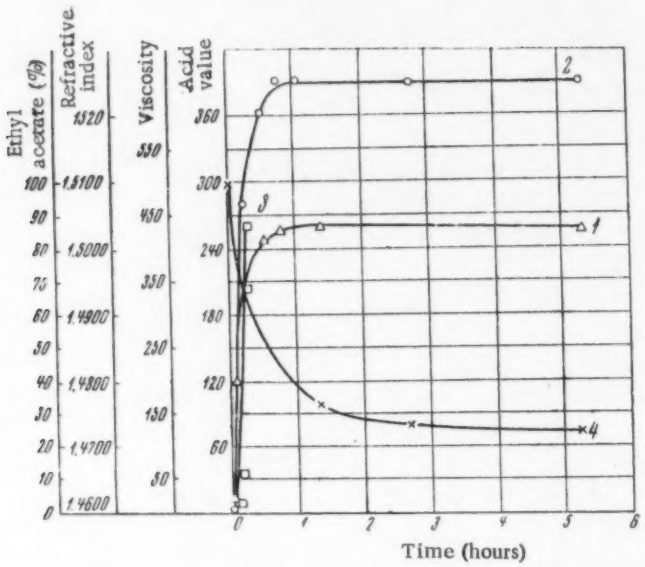

Fig. 5. Reaction between diethoxymethylphenylsilane and boron triacetate: 1) amount of ethyl acetate eliminated (%); 2) refractive index; 3) viscosity (centipoise); 4) acid value.

Investigation of the stability of the Si—O—B linkage of the polymethylphenylborosiloxanes obtained toward the action of aqueous acids and alkalis showed that this linkage is readily broken down with liberation of boric acid and formation of an organosilicon polymer by the reaction

$$x\,(-\mathrm{SiR_2O-B(OC_4H_9)-OSiR_2O-}) + \mathrm{H_2O} \xrightarrow[\mathrm{H^+}]{\mathrm{OH'}} (-\mathrm{SiR_2OSiR_2O-})_x + \mathrm{B(OH)_3} + \mathrm{C_4H_9OH}.$$

EXPERIMENTAL

The following substances were used in the investigation: chlorotrimethylsilane, b.p. 56-58°, 32.5% Cl; ethoxytrimethylsilane, b.p. 75°, n_D^{20} 1.3740; acetoxytrimethylsilane, b.p. 102-105°, n_D^{20} 1.388; diethoxymethylphenylsilane, b.p. 75-78° (4 mm); dibutoxymethylphenylsilane, b.p. 116-120° (8 mm), n_D^{20} 1.4640; diacetoxymethylphenylsilane, b.p. 127-130° (6 mm), 50.1% CH_3COO; diethoxydimethylsilane, b.p. 111-114°, n_D^{20} 1.3840; dibutoxydimethyl-silane, b.p. 190-192°, n_D^{20} 1.4040; diacetoxydimethylsilane, b.p. 59-64° (10 mm), n_D^{20} 1.4045; boric acid. commercial quality.

1. Preparation of Tributyl Borate. Tributyl borate was prepared by the method described in the collection [5]. A mixture of 43.4 g (0.7 mole) of boric acid and 220 g (3.0 moles) of butyl alcohol was prepared in a Favorsky flask fitted with fractionation column. The reaction mixture was heated, and a mixture of water and butyl alcohol was distilled off. When water had been completely removed, the reaction mixture was vacuum-

fractionated and gave 145- g of product, b.p. 99-100° (9 mm).

2. Preparation of Boron Triacetate. Boron triacetate was prepared by the method described in the collection [6]. A mixture of 30 g of boric acid and 160 g of acetic anhydride was prepared in a flask fitted with reflux condenser. The reaction mixture was slowly heated to 60° and maintained at that temperature for five hours. The reaction product was set aside overnight so that it would cool slowly. On the next day a white crystalline precipitate had formed. It was filtered off and dried in a vacuum desiccator (80 g, m.p. 119°).

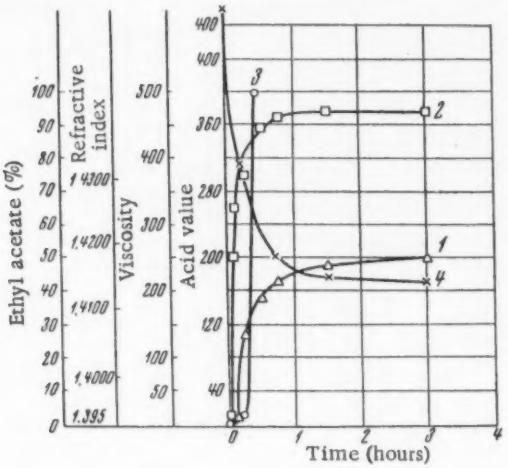

Fig. 6. Reaction between diethoxydimethylsilane and boron triacetate: 1) refractive index; 2) amount of ethyl acetate eliminated (%); 3) viscosity (centipoise); 4) acid value.

3. Condensation of Diacetoxymethylphenylsilane with Tributyl Borate. A mixture of 71.1 g (0.3 mole) of diacetoxymethylphenylsilane and 45.9 g (0.2 mole) of tributyl borate was prepared in a three-necked flask fitted with thermometer, oil-sealed stirrer, tube leading to a receiver for the collection of volatile reaction products, and tube for the taking of samples from the reaction flask during the reaction. The reaction flask was placed in an oil bath at 170°. The temperature in the reaction flask was maintained constant within ± 5° throughout the experiment. The experiment was stopped when butyl acetate ceased to be driven off; periodic measurements of the amount of butyl acetate eliminated were made during the reaction. For the condensation product we determined a) viscosity (centipoise) with the aid of an Ostwald capillary viscometer; b) refractive index with an Abbe refractometer; c) acid value.

The butyl acetate obtained was distilled, and it then had b.p. 118-124°, n_D^{20} 1.3952, d_4^{20} 0.898, and 50.5% CH_3COO. For butyl acetate the literature gives b.p. 125°, n_D^{20} 1.3951; d_4^{20} 0.881, and 50.8% CH_3COO.

Reaction between diacetoxydimethylsilane and tributyl borate was carried out similarly. The components taken for reaction, the reaction temperature, and the duration of condensation are listed in Table 1.

4. Condensation of Dibutoxymethylphenylsilane with Boron Triacetate. The reaction was carried out in the apparatus used in the previous experiments. The flask contained 79.8 g (0.3 mole) of dibutoxymethylphenylsilane and 37.5 g (0.2 mole) of boron triacetate, and the flask was placed in an oil bath at 170°. The butyl acetate eliminated was collected. The condensation product was a viscous homogeneous polymer which rapidly became white at the surface when exposed to air.

The reactions between boron triacetate and diethoxymethylphenylsilane, dibutoxydimethylsilane, and diethoxydimethylsilane were carried out similarly. Reaction temperatures, times of condensation, and the reactants are listed in Table 2. The results of the condensation experiments are presented in Figures 1-6.

The ethyl acetate obtained in the condensation reaction was fractionated and then had b.p. 75-80°, n_D^{20} 1.3750; and d_4^{20} 0.910. For ethyl acetate the literature gives b.p. 77.15°; n_D^{20} 1.3722; and d_4^{20} 0.9003.

TABLE 1

Experiment	Reactants	Molar ratio of reactants	Reaction temperature (°C)	Duration of heating (hours)	Amount of butyl acetate eliminated (%)
1	$(CH_3)_2Si(OCOCH_3)_2$ and $B(OC_4H_9)_3$	0.3 0.2	170	14	74.8
2	$(CH_3)C_6H_5Si(OCOCH_3)_2$ and $B(OC_4H_9)_3$	0.3 0.2	170	13	75.7

TABLE 2

Experiment	Reactants	Molar ratio of reactants	Reaction temperature (°C)	Duration of heating (hours)	Amount of alkyl acetate eliminated (%)
1	$(CH_3)C_6H_5Si(OC_4H_9)_2$ and $B(OCOCH_3)_3$	0.3 0.2	170	24	57.0
2	$CH_3(C_6H_5)Si(OC_2H_5)_2$ and $B(OCOCH_3)_3$	0.3 0.2	170	5.5	86.5
3	$(CH_3)_2Si(OC_4H_9)_2$ and $B(OCOCH_3)_3$	0.3 0.2	170	12	60.8
4	$(CH_3)_2Si(OC_2H_5)_2$ and $B(OCOCH_3)_3$	0.3 0.2	170	3	94.0

5. Determination of the Stability of the Si—O—B Linkage in the Polymer obtained from Diacetoxymethylphenylsilane and Tributyl Borate. A solution in 12 g of acetone of 3 g of the polymer obtained by condensation of diacetoxymethylphenylsilane with tributyl borate at a molar ratio of 3: 2 was added with stirring to 10 g of 0.1 N NaOH at 20°. Ether was added to the polymer-water mixture in order to improve the separation of the aqueous layer. The ethereal solution of polymer was separated from the aqueous layer and washed until the reaction for OH' with phenolphthalein was negative; ether was evaporated off. The resulting polymer was analyzed, and the analysis showed that the polymer did not contain boron. Water was evaporated from the aqueous layer, and a white substance remained at the bottom of the dish. Qualitative analysis of this substance showed that it contained much boron, but no silicon.

When hydrolyzed similarly in neutral and acid media, the Si—O—B linkage of the polymer was again broken and the polymer obtained after hydrolysis contained no boron; all the boron was found in the aqueous layer.

SUMMARY

New polymers - polyorganoborosiloxanes, the molecular chain of which contains silicon-oxygen-boron linkages - were prepared by the heterofunctional condensation of alkyl- and aryl-dialkoxysilanes with boron triacetate and of alkyl- and aryl-diacetoxysilanes with tributyl borate.

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SYNTHESIS AND PROPERTIES OF SOME VINYL-, PHENYL-, AND ALKYL-SILANES CONTAINING SILICON-ATTACHED HYDROGEN. STABILIZING EFFECT OF CHLOROSILYL GROUPS

A. D. Petrov, V. A. Ponomarenko, B.A. Sokolov, and Yu. P. Egorov

In a series of communications [1-4] we have shown that it is possible to synthesize various substituted silanes containing silicon-attached hydrogen by reduction of the corresponding chlorosilanes with lithium hydride. In this way we prepared allylsilanes, (chloroalkyl) silanes, and other mono-, di-, and trisilanes. In the present investigation we extended the method of reduction with lithium hydride to various vinyl- and aryl-chlorosilanes. We were interested in the possibility of using lithium hydride not only for the reduction of compounds containing three silicon-attached chlorines, but also for the reduction of compounds containing less than three such chlorines.

We prepared chlorovinylsilanes by dehydrochlorination of alkylchloro(2-chloroethyl)silanes with the aid of quinoline:

$$R_2SiCH_2CH_2Cl \xrightarrow{\text{quinoline}} R_2SiCH=CH_2,$$
$$\quad\quad\quad

Replacement of silicon-attached chlorine atoms by any other radicals makes the C – Cl bond in $Cl_3SiCH_2CH_2Cl$ both more reactive and at the same time more prone to β-decomposition. As Petrov and Mironov [9] showed, in the reaction of $Cl_3SiCH_2CH_2Cl$ with RMgX the relative extents of β-decomposition and replacement of Cl by R are determined mainly by the activity of the Grignard reagent. Similar stabilizing effects are shown also by other electronegative groups, such as OR and OCOR [10], and O – Si ≡ [11].

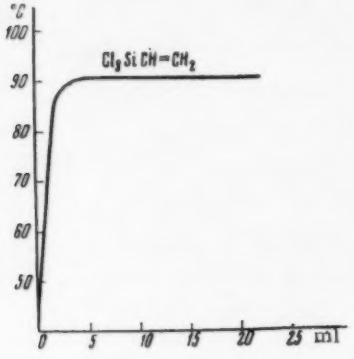
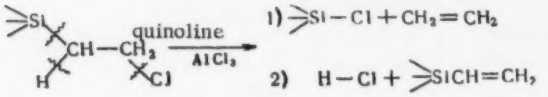


Fig. 1.

The dehydrochlorination of our alkylchloro (2-chloroethyl)silanes with the aid of quinoline was always accompanied by a β-decomposition side reaction (Fig. 2-5) except in the case of $Cl_3SiCH_2CH_2Cl$ (Fig. 1). $Cl_3SiCHClCH_2SiCl_3$, which has two trichlorosilyl groups, is also stable to β-decomposition; $SiCl_4$ - and evidently also trichlorovinylsilane, indicated by a small inflection on the fractionation curve - is formed in very small amount (Fig. 2). Hence, in the series $R_3SiCH_2CH_2Cl$, $R_2SiClCH_2CH_2Cl$, $RSiCl_2CH_2CH_2Cl$, and $SiCl_3CH_2CH_2Cl$, as chloride atoms accumulate on the silicon atom, i.e., as the stabilizing effect of Si – Cl groups increases, the reaction of β-decomposition gradually gives way to the reaction of dehydrochlorination. The relative extents of the two reactions depend not only on the structure of the original halogen compound, but also on the nature of the dehydrochlorination reagent and the reaction conditions. The direction in which the transformation of the β-halo compound proceeds depends on which of the bonds in the β-position with respect to the C – Cl bond (Si – C or C – H) is broken first under the given concrete conditions.



It is interesting that $Cl_3SiCH_2CH_2Cl$ undergoes these two reactions simultaneously even at 600° without dehydrochlorination agent [12]. The stabilizing effect of Si – Cl groups leads to strengthening of all bonds in the alkyl radical and particularly of the Si – C bond. In the light of this discussion it can be understood why the activity of chloro(chloroalkyl) silanes in the Friedel-Crafts reaction diminishes as the number of silicon-attached chlorines increases and as the reacting bond becomes closer to the chlorosilyl groups *, i. e., as Petrov, Chernyshev, and Dolgaya [6] have shown, in the series $C_2H_5SiCl_2CH_2CH_2Cl$ > $Cl_3SiCH_2CH_2Cl$ > $Cl_3SiCHClCH_3$ > Cl_3SiCH_2Cl > $Cl_3SiCHCl_2$ > $Cl_3SiCHClSiCl_3$, in $Cl_3SiCHClSiCl_3$ the effect of the two trichlorosilyl groups is so strong that it does not undergo the Friedel-Crafts reaction even under very severe conditions. As would be expected, in the dehydrochlorination of chloro (1- and 2- chloroethyl) silanes the effect of chlorosilyl groups is manifested more strongly in the 1-chloroethyl compounds than in the 2-chloroethyl compounds. As can be seen from Figures 3 and 5, in the dehydrochlorination of mixtures of chloro (1- and 2-chloroethyl) ethylsilanes and of chloro (1- and 2-chloroethyl)diethylsilanes, the 1-chloroethyl compounds were to a considerable extent recovered unchanged. In this case the stabilizing effect of chlorosilyl groups is analogous to be effect of the trifluoromethyl group in the dehydrochlorination of 2-chloro-1,1,1-trifluoropropane ($F_3CCHClCH_3$) and of 3-chloro-1,1,1-trifluoropropane ($F_3CCH_2CH_2Cl$) [13].

Hence, the resemblance which we noted previously in the orienting effects of the groups $SiCl_3$ and CF_3 in chlorination [14] is to be paralleled in an analogous stabilizing effect in dehydrochlorination, alkylation, and other reactions of chloro (1- and 2-chloroalkyl) silanes.

The alkylchlorovinylsilanes obtained in this way, and also trichloro (α-methylbenzyl)-, trichlorophenethyl-, and some chlorodialkyl-silanes, were readily reduced by lithium hydride. It is interesting that reduction in dioxane generally proceeded more readily than in dibutyl or diisopentyl ether in spite of the lower temperature of the reaction

* Approximately the same effect is found also in the reaction of chloro (1- and 2-chloroalkyl) silanes with silicon under the conditions of direct synthesis [8].

medium. The physical properties of all the compounds that we prepared are given in Table 1.

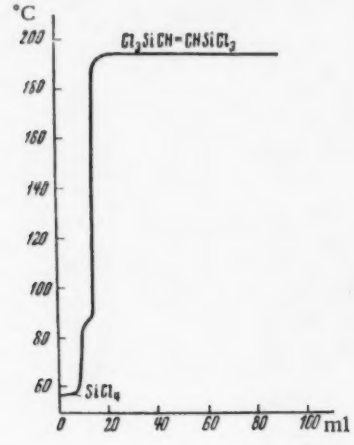


Fig. 2

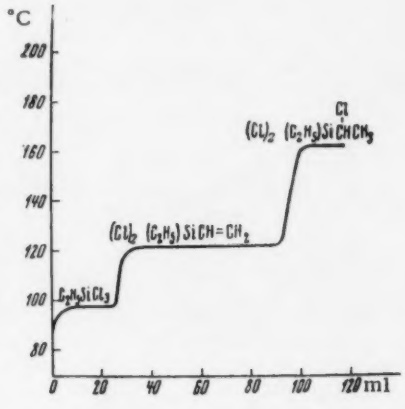


Fig. 3

In conclusion we will discuss the peculiar features of the Raman spectra of some of the silanes that we prepared. In the papers [15] and [16] physical spectroscopic data were given which indicated the "barrier" character of the silicon atom, which was manifested by reduction or even elimination of interaction through the silicon atom of vibrational coordinates in radicals attached to silicon. One manifestation of this property is the

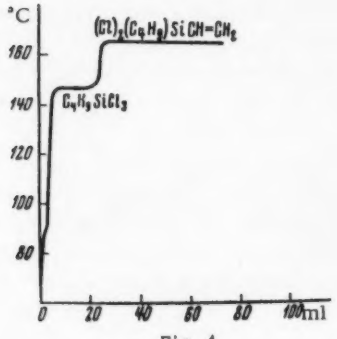


Fig. 4

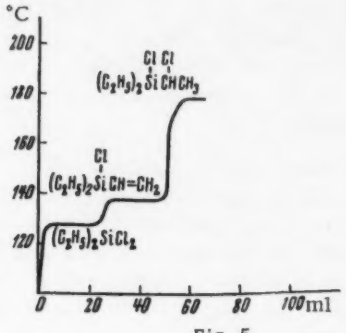


Fig. 5

coincidence of the symmetrical and antisymmetrical frequencies of Si –H in R_2SiH_2 and $RSiH_3$ observed in the investigations [17] and [18]. In the Raman and infrared spectra a broad band of complex structure is always observed when R is an alkyl radical. As there can be no doubt that H – Si –H forms a tetrahedral angle, this can be observed only when the coefficient of interaction between contiguous Si–H bonds is zero [19]. Let us examine the experimental values of valency vibration frequencies ν (Si –H) and deformation frequencies δ (H –Si –H) obtained in this (for (I) – (IX)) and other investigations [17, 20]. These data are presented in Table 2; Column 1 of this table gives the frequencies of SiH_4 [21].

The mean value of the frequency (cm^{-1}) of the valency vibrations rises successively from ≡ SiH (2120 ± 5), through $=SiH_2$ (2135 ± 5) and $-SiH_3$ (2155 ± 5), to SiH_4 (2180) •, and the value of the deformation frequency remains constant at about 950 in all groups (in SiH_4 the mean of the symmetrical and threefold degenerate frequencies is 948).

• The same conclusion was reached in a recently published investigation of Batuev [26].

TABLE 1

No.	Formula of compound	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	MR Found	MR Calculated
1	$CH_2=CHSiH_2(C_2H_5)$	47 (742)	1.4030	0.6940	30.30	30.33
2	$CH_2=CHSiH(C_2H_5)_2$	100—100.5 (748)	1.4210	0.7384	39.23	39.33
3	$CH_2=CHSiH_2(C_4H_9)$	103 (753)	1.4189	0.7329	39.35	39.47
4	$C_6H_5-CHSiH_3$ | CH_3	163.8 (743)	1.5130	0.8831	46.32	46.19
5	$C_6H_5-CH_2CH_2SiH_3$	171.5 (743)	1.5109	0.8824	46.21	46.19
6	$i\text{-}C_4H_9SiH_2(CH_3)$	73.3 (749)	1.3976	0.6941	35.51	35.43
7	$i\text{-}C_4H_9SiH_2(C_2H_5)$	103.7 (748)	1.4100	0.7166	40.19	40.06
8	$(i\text{-}C_4H_9)(CH_3)SiHCl$	112.5 (757)	1.4170	0.8642	39.77	39.43
9	$(i\text{-}C_4H_9)(C_2H_5)SiHCl$	140 (743)	1.4281	0.8844	43.85	44.06
10	$(C_6H_5)(Cl)_2SiCH=CH_2$	165.5 (750)	1.4481	1.0320	47.52	47.59
11	$(C_6H_5)(Cl)_2SiCH_2CH_2Cl$	80—81 (6)	1.4649	1.1496	52.82	52.90
12	$C_6H_5Si(Cl)_2CH_2CH_2Cl$	116.5 (6)	1.5445	1.2771	59.09	58.71

Taking account of the low interaction between Si − H bonds and the considerable mass of the silicon atom as compared with that of the hydrogen atom, we estimated the force constants of Si− H bonds from the usual equation:

$$\nu^2 = \frac{f}{M}, \text{ where } \frac{1}{M} = \left(\frac{1}{m_{Si}} + \frac{1}{m_H}\right),$$

(M is the reduced mass, ν is the frequency, and f is the force constant of Si −H). Assuming that f_{Si-H} for the group ≡ Si−H is unity, we may determine the proportionality (1 : 1.015 : 1.03 : 1.06) expressing the variation of this quantity. The numerical values obtained vary in a definite way - in accordance with a geometric progression starting from the second term. The constancy of the deformation frequency enables us to assert that the quasielastic forces preventing change in the H−Si −H angle do not depend on the number of Si −H bonds. It is interesting that an analogous conclusion for HCH angles in CH_3 and CH_4 were obtained previously [19 (Vol. 1, p. 370)].

Our results on the force constants f_{Si-H} permit us to consider (taking the similar structures of the electron shells of Si and C into account) the possibility of an analogous relationship for the C −H bonds in alkanes. Support for this view can be found in the results obtained in the investigation [18] for the force constant f_{C-H} of the C−H bond in CH_4 and CH_3 - namely, 8.34 and $8.08 \cdot 10^{-6}$ cm² respectively. The second constant is 0.97 of the first; in the silanes the corresponding ratio is 0.975. Further consideration of this matter requires the knowledge of the positions of the frequencies of the groups CH_3, CH_2, and CH, the determination of which is at present difficult.

We also wish to discuss the characteristics of some frequencies in the spectra of (I) − (V). (I) and (II) contain a vinyl group, the characteristic frequencies of which - 1272, 1406, 1595, and 3054 cm^{-1} - are in accord with values found previously [22]. We may note the frequencies of Si-attached C_2H_5 - 975, 1020, 1236, and 1465 cm^{-1} [23]. (IV) and (V) contain a monosubstituted aromatic ring, and their spectra contain the usual frequencies of this grouping - 620, 1002, 1031, 1205, 1600, 3030, 3051, and 3065 cm^{-1}. No substantial difference was found in the positions of these frequencies in (IV) and (V). One difference that could be observed was a greater ratio of the intensities of the 1600 and 1000 lines in (IV) (0.55) than in (V) (0.35). Intensities were measured photometrically at the maxima of the lines. The ratio 0.35 for (V) is close to that generally found in monosubstituted aromatic compounds; for example, Shorygin obtained 0.35 for toluene [24]. An increased ratio was found in the investigation cited when the double bonds of the ring were conjugated with C =C bonds, the increase being 1.3-2.4. In the case of (IV) we probably encountered the phenomenon of intermolecular action as observed previously in the investigation [16] for alkenylsilanes.

TABLE 2

	SiH_4	$-SiH_3$						$>SiH_2$					$\equiv SiH$			
	SiH_4	(IV)	(V)	(VI)	(X)	(XI)	(XII)	(II)	(III)	(VI)	(VII)	(XIII)	(I)	(VIII)	(IX)	(XIV)
ν(Si—H)	2175(Raman) 2183 (infrared)	2150	2152	2155	2161	2157	2152	2136	2135	2133	2140	2127	2115	2120	2125	2118
δ(H--Si—H)	987 (Raman) 910 (infrared)	941	946	954	948	943	946	942	954	954	956	949				
Average ν(Si—H)	~2180 cm^{-1}			2155±5					2135±5				2120±5			

$(C_2H_5)_2HSiCH{=}CH_2$ (I)

$(C_2H_5)H_2SiCH{=}CH_2$ (II)

i-$C_4H_9SiH_2(CH_3)$ (III)

$C_6H_5{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}SiCH_3$ (IV)

$C_6H_5CH_2CH_2SiH_3$ (V)

$(CH_3)H_2SiCH_2SiH_3$ (VI)

$CH_3\overset{H_2}{\underset{|}{Si}}CH_2{-}\overset{H_2}{\underset{|}{Si}}{-}CH_2\overset{H_2}{\underset{|}{Si}}CH_3$ (VII)

$(C_3H_5)_2HSi(i\text{-}C_4H_9)$ (VIII)

$(C_3H_5)_2HSiCH_3$ (IX)

$H_3SiCH_2SiH_3$ (X)

$H_3SiCH_2CH_2SiH_3$ (XI)

$C_6H_{13}SiH_3$ (XII)

$(C_3H_7)_2SiH_2$ (XIII)

$(CH_3)_3SiH$ (XIV)

$(C_2H_5)_2HSiCH{=}CH_2$(I), ν в $см^{-1}$: 174 (3), 313 (4ш), 342 (0), 512 (1), 595 (10), 690 (2ш), 715 (2ш), 822 (5ш), 975 (4), 1022 (4), 1107 (2), 1179 (0), 1236 (5), 1274 (5), 1406 (6), 1420 (4), 1465 (5), 1595 (5р), 2115 (8ш), 2879 (7р), 2895 (7р), 2918 (7р), 2942 (3), 2968 (4), 2975 (7р), 3054 (5).

$(C_2H_5)H_2SiCH{=}CH_2$ (II), ν в $см^{-1}$: 169 (2), 313 (5ш), 585 (2), 620 (5ш), 674 (4), 712(2), 764 (3ш), 845 (2), 942 (5ш), 973 (2), 1022 (3ш), 1108 (1), 1235 (3), 1270 (5), 1406(6), 1420 (1), 1462 (3), 1595 (5р), 2136 (10ш), 2877 (5р), 2899 (5р), 2916 (1), 2961 (1), 2978 (7), 3054(3).

t-$C_4H_9SiH_2(CH_3)$ (III), ν в $см^{-1}$: 170 (2), 240 (3), 350 (4), 425 (3), 600 (2ш), 636 (2), 655 (5), 690 (4), 700 (4), 765 (3ш), 808 (3), 832 (3), 954 (5ш), 1050 (2ш), 1092 (2), 1219 (4), 1260 (2), 1332 (3ш), 1420 (1), 1450 (4), 1464 (4), 2135 (10ш), 2872 (10), 2909 (10), 2934 (2), 2964 (10).

$C_6H_5{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}SiH_3$ (IV), ν в $см^{-1}$: 170 (2), 410 (3ш), 485 (2), 622 (5), 650 (2), 701 (3ш), 771 (2), 792 (3), 941 (4), 964 (2), 1002 (10), 1033 (4), 1116 (2), 1160 (4), 1182 (3), 1202 (5), 1460 (2дв), 1601 (6р), 2150 (10ш), 2873 (4), 2883 (2), 2930 (3), 2960 (4), 3030 (2), 3051 (6), 3063 (6).

$C_6H_5{-}CH_2CH_2SiH_3$ (V), ν в $см^{-1}$: 167 (3), 200 (4ш), 277 (2), 485 (3ш), 562 (2), 616 (5дв), 648 (0), 697 (2ш), 732 (2), 758 (3), 824 (4р), 946 (5ш), 1002 (10), 1031 (5), 1159 (3), 1182 (3), 1206 (5), 1325 (2), 1410 (3), 1452 (2ш), 1584 (2), 1600 (4р), 2152 (10ш), 2853 (3ш), 2895 (5), 2918 (3ш), 3035 (4), 3050 (8), 3065 (6).

[Publisher's note: 'B' ≡ the word 'in'; 'ω' ≡ 'b', 'p' ≡ 'sh', and 'ДВ' ≡ 'db' (Raman spectra intensity symbols).]

EXPERIMENTAL

Butyldichloro (2-chloroethyl)silane. A solution of butylmagnesium bromide prepared from 137 g of butyl bromide and 24 g of magnesium in 300 ml of dry ether was added dropwise to a stirred solution of 198 g of $Cl_3SiCH_2CH_2Cl$ in 100 ml of ether. The precipitate was filtered off, ether was distilled off, and vacuum fractionation of the residue gave 103 g (47%) of $C_4H_9Si(Cl)_2CH_2CH_2Cl$, b.p. 80-81° (6 mm); d_4^{20} 1.1496; n_D^{20} 1.4649; found MR 52.82; calculated MR 52.90.

Found %: C 32.98; 33.03; H 6.02; 6.03; Cl 48.33; 48.67; Si 12.33; 12.91 $C_6H_{13}SiCl_3$. Calculated %: C 32.81; H 5.97; Cl 48.44; Si 12.78

Dichloro (2-chloroethyl)phenylsilane. A solution of phenylmagnesium bromide prepared from 158 g of bromobenzene and 23.5 g of magnesium in 300 ml of dry ether was added dropwise to 198 g of $Cl_3SiCH_2CH_2Cl$ in 100 ml of ether. The reaction mixture was left overnight. The precipitate was filtered off, ether was distilled off, and vacuum fractionation of the residue gave 111 g of $C_6H_5Si(Cl)_2CH_2CH_2Cl$, b.p. 116.5° (6 mm); d_4^{20} 1.2771; n_D^{20} 1.5445; found MR 59.09; calculated MR 58.71.

Trichlorovinylsilane.* Trichloro (2-chloroethyl)silane (66 g) was dehydrochlorinated with the aid of quinoline (45 g). Fractionation of the reaction products through a column (Fig. 1) gave 25 g (46.4%) of trichlorovinylsilane, b.p. 90.5° (752 mm); d_4^{20} 1.2335; n_D^{20} 1.4349; found MR 33.08; calculated MR 32.89.

1,1,1,4,4,4-Hexachloro-1,4-disilabut-2-ene. The compound $Cl_3SiCH(Cl)CH_2SiCl_3$ was prepared in 96% yield by the chlorination of $Cl_3SiCH_2CH_2SiCl_3$ in the apparatus described previously [25], and 240 g of it was dehydrochlorinated with the aid of 150 g of quinoline. Fractionation through a 35-plate column (Fig. 2) gave 98 g (46%) of $Cl_3SiCH{=}CHSiCl_3$, b.p. 193.5° (752 mm). In addition, 15 g of $SiCl_4$, the β-decomposition product, was obtained.

Butyldichlorovinylsilane. A mixture of 131 g of butyldichloro (2-chloroethyl)silane and 90 g of quinoline was heated for three hours in a flask fitted with fractionation column, and the dehydrochlorination product was distilled from the quinoline and redistilled through a 35-plate column (Fig. 4). The product, amounting to 51 g (46.8 %), was $CH_2{=}CHSi(Cl)_2C_4H_9$, b.p. 165.5° (750 mm); d_4^{20} 1.0320; n_D^{20} 1.4481; found MR 47.52; calculated MR 47.59.

Found %: C 39.47; 39.54; H 6.54; 6.77 Cl 38.96; 38.51; Si 15.14; 15.23 $C_6H_{12}SiCl_2$. Calculated %: C 39.35 H 6.61; Cl 38.72; Si 15.32

* The dehydrochlorination of trichloro (2-chloroethyl)silane was carried out by A. D. Snegova.

Apart from $C_4H_9(Cl)_2SiCH=CH_2$, 17.5 g of $C_4H_9SiCl_3$, b.p. 147.5° (751 mm) was obtained.

Dichloroethylvinylsilane. A mixture of dichloro (1- and 2-chloroethyl)ethylsilanes (184 g) obtained by the chlorination of dichlorodiethylsilane [4] was dehydrochlorinated with the aid of 120 g of quinoline. The reaction conditions were similar to those described above. Fractionation through a 35-plate column (Fig. 5) gave 60 g (40%) of dichloroethylvinylsilane, b.p. 122° (744 mm). In addition, 32 g of the β-decomposition product-trichloroethylsilane, b.p. 97.7° (741 mm) and 18 ml of unchanged dichloro (1-chloroethyl) ethylsilane, b.p. 161.5° (744 mm), were isolated.

Chlorodiethylvinylsilane. A mixture of chloro (1- and 2- chloroethyl)-diethylsilanes (85 g) obtained by the chlorination of chlorotriethyl-silene [4] was dehydrochlorinated. Fractionation through a 35-plate column (Fig. 3) gave 22 g (32%) of chlorodiethylvinylsilane, b.p. 138° (736 mm). In addition, 27 g of the β-decomposition product-dichlorodiethylsilane, b.p. 127° (733 mm) - and 8 ml of unchanged chloro (1-chloroethyl) diethylsilane, b.p. 178° (736 mm), were isolated.

Chloroisobutylmethylsilane. The Grignard reagent prepared from 184 g of isobutyl iodide and 24 g of magnesium in 300 ml of absolute ether was added dropwise to a stirred solution of 115 g of dichloromethylsilane in 125 ml of ether. The reaction mixture was heated in a water bath for four hours. The precipitate was filtered off, ether was distilled off, and distillation of the residue through a 35-plate column gave 43 g (31.6%) of chloroisobutylmethylsilane, b.p. 112.5° (737 mm); d_4^{20} 0.8642; n_D^{20} 1.4170; found MR 39.77; calculated MR 39.43.

Found %: C 43.81; 44.02; H 9.87; 9.75; Cl 23.99; 23.93; Si 20.74; 20.65 $C_5H_{13}SiCl$. Calculated %: C 43.94; H 9.59; Cl 25.94; Si 20.53

Chloroethylisobutylsilane. A solution of isobutylmagnesium iodide prepared from 184 g of isobutyl iodide and 24 g of magnesium in 300 ml of ether was added dropwise to a stirred solution of 129 g of dichloroethylsilane in 125 ml of ether. The precipitate was filtered off, ether was distilled off, and fractionation through a 35-plate column gave 44 g (23.9%) of chloroethylisobutylsilane, b.p. 140° (743 mm); d_4^{20} 0.8844; n_D^{20} 1.4281; found MR 43.85; calculated MR 44.06.

Found %: C 47.55; 47.52; H 10.04; 9.95; Cl 23.50; 23.32; Si 18.39; 18.09 $C_6H_{15}SiCl$. Calculated %: C 47.82; H 10.03; Cl 23.53; Si 18.62

Ethylvinylsilane. This was prepared by the reduction of 62 g of dichloroethylvinylsilane by 24 g of LiH in 80 ml of diisopentyl ether under the conditions described previously [1]. Distillation of the reaction products through a 35-plate column gave 17 g (38.8%) of ethylvinylsilane, b.p. 47° (742 mm); d_4^{20} 0.6940; n_D^{20} 1.4030; found MR 30.30; calculated MR 30.33.

Found %: C 55.51; H 12.21; Si 32.18 $C_4H_{10}Si$. Calculated %: C 55.74; H 11.70; Si 32.56

Diethylvinylsilane. Under the conditions of the previous experiment 22 g of chlorodiethylvinylsilane and 4 g of LiH in 20 ml of diisopentyl ether gave (fractionation through 35-plate column) 3.3 g (20%) of diethylvinylsilane, b.p. 100-100.5° (748 mm); d_4^{20} 0.7384; n_D^{20} 1.4210; found MR 39.23; calculated MR 39.33.

Found %: C 63.24; 63.34; H 12.34; 12.45; Si 24.59; 24.56 $C_6H_{14}Si$. Calculated %: C 63.08; H 12.36; Si 24.56

Butylvinylsilane. Under the conditions described above, 57 g of butyldichlorovinylsilane and 15 g of LiH in 70 ml of diisopentyl ether gave (fractionation through 35-plate column) 1.1 g of butylvinylsilane, b.p. 103° (753 mm); d_4^{20} 0.7329; n_D^{20} 1.4189; found MR 39.35; calculated MR 39.47.

Found %: C 63.86; 63.65; H 12.80; 12.95; Si 22.67; 22.51 $C_6H_{14}Si$. Calculated %: C 63.08; H 12.36; Si 24.56.

Isobutylmethylsilane. Reduction of 47 g of chloroisobutyl-methylsilane with 25 g of LiH in 70 ml of diisopentyl ether was carried out in a metal reactor fitted with stirrer, dropping funnel, and fractionation column. The reduction product was distilled off continuously through the column. Refractionation gave 14 g (40%) of isobutylmethylsilane, b.p. 73.3° (749 mm); d_4^{20} 0.6941; n_D^{20} 1.3976; found MR 35.51; calculated MR 35.43.

Found %: C 59.01; 58.84; H 13.69; 13.84; Si 27.40; 27.20 $C_5H_{14}Si$. Calculated %: C 58.74; H 13.81; Si 27.45

Ethylisobutylsilane. Under the conditions of the preceding experiment, reaction of 45 g of chloroethylisobutylsilane with 7.2 g of LiH gave 6.5 g (18.7%) of ethylisobutylsilane, b.p. 103.7° (748 mm); d_4^{20} 0.7166; n_D^{20} 1.4100; found MR 40.19; calculated MR 40.06.

Found %: C 61.84; 61.80; H 13.78; 13.77; Si 24.18; 24.25 $C_6H_{16}Si$. Calculated %: C 61.99; H 13.87; Si 24.14

(α-Methylbenzyl)silane and Phenethylsilane. Under the conditions of the two preceding experiments, reaction of 100 g of a mixture of trichloro (α-methylbenzyl)- and trichlorophenethyl-silanes (prepared as described previously [5, 6]) with 30 g of LiH in 150 ml of dioxane gave (two fractionations through a 35-plate column) gave two fractions. Fraction I (5.7 g) was (α-methylbenzyl)silane, b.p. 163.8° (743 mm); d_4^{20} 0.8831; n_D^{20} 1.5130; found MR 46.32; calculated MR 46.19.

Found %: C 69.99; 70.19; H 9.05; 9.24; Si 20.51; 20.56 $C_8H_{12}Si$. Calculated %: C 70.59; H 8.82; Si 20.59

Fraction II (9.3 g) was phenethylsilane, b.p. 171.5° (743 mm); d_4^{20} 0.8824; n_D^{20} 1.5109; found MR 46.21; calculated MR 46.19.

Found %: C 70.45; 70.43; H 8.97; 8.80; Si 20.29; 20.11 $C_8H_{12}Si$. Calculated %: C 70.59; H 8.82; Si 20.59

SUMMARY

1. Reduction of vinyl-, phenyl-, and alkyl-chlorosilanes with the aid of lithium hydride gave various vinyl-, phenyl-, and alkyl-silanes.

2. The Raman spectra of compounds of formula $HSiR_3$, H_2SiR_2, and H_3SiR (R is an aliphatic radical) show that the quasielastic constant of the Si – H bond diminishes as the number of silicon-attached hydrogen atoms diminishes.

3. The dehydrochlorination of some alkyl (2-chloroethyl)silanes and an analogous disilabutane derivative was studied, and it was shown that there is a relationship between the dehydrochlorination reaction and the accompanying β-decomposition reaction.

4. It was shown that chlorosilyl groups have a stabilizing action in the dehydrochlorination reaction and, as chlorine atoms accumulate on silicon, the yield of β-decomposition products falls and the yield of dehydrochlorination products rises; there is also a reduction in the reactivity of α-chloro compounds.

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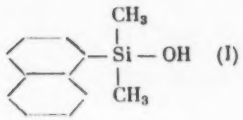
SYNTHESIS AND REACTIONS OF OXYGEN-CONTAINING ORGANOSILICON COMPOUNDS

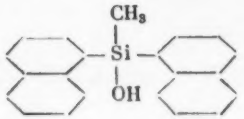
COMMUNICATION 7. SYNTHESIS OF DIMETHYL-1-NAPHTHYL-, METHYLDI-1-NAPHTHYL-, ETHYLDI-1-NAPHTHYL- AND TRI-1-NAPHTHYL-SILANOLS

M. F. Shostakovsky and Kh. I. Kondratyev

In the development of the chemistry of vinyl ethers, the investigation of their reactions with silanols is of importance [1-3]. There are descriptions in literature of a fairly large number of silanols of the aliphatic, aliphatic-aromatic, and aromatic series, i.e., of general formula $Ar_nAlk_{3-n}SiOH$, in which n = 0, 1, 2, or 3, Alk = CH_3, C_2H_5, C_3H_7, C_4H_9, C_5H_{11}, $CH_2=CH$, $CH\equiv C$, and others, and Ar = C_6H_5, $C_6H_5CH_2$, and others containing C_6H_5, but not the naphthyl radical.

The present investigation forms a continuation of our investigations on the synthesis and reactions of silanols and silanediols of the aliphatic-aromatic series [3, 4], and it is devoted to the description of silanols containing naphthyl radicals. In the present paper we describe dimethyl-1-naphthylsilanol (I), methyldi-1-naphthylsilanol (II) ethyldi-1-naphthylsilanol (III), and tri-1-naphthylsilanol (IV), i.e.,


(I)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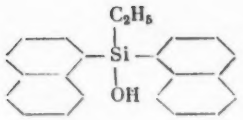
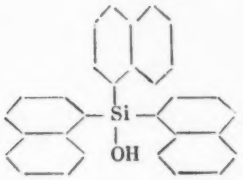
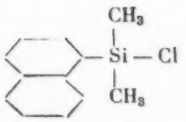
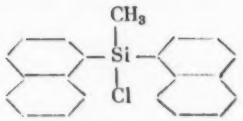
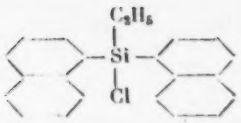

(III)


(IV)

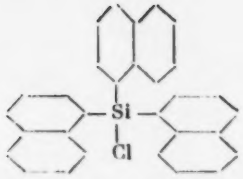
The starting materials for the preparation of (I) - (IV) were the corresponding halosilanes: chlorodimethyl-1-naphthylsilane (V), chloromethyldi-1-naphthylsilane (VI), chloroethyldi-1-naphthylsilane (VII), and chlorotri-1-naphthylsilane (VIII):


(V)


(VI)



(VII)



(VIII)

The halosilanes were prepared by two methods : a) via organomagnesium compounds; b) via organolithium compounds. (V) was prepared only by the first method [5]; (VI) by the first and second [4]; and (VII) and (VIII) only by the second method [4].

The synthesis of the chloro compounds (V) and (VI) via organomagnesium compounds followed the scheme:

$$C_{10}H_7MgBr + (CH_3)_2SiCl_2 \rightarrow C_{10}H_7-\underset{\underset{CH_3}{|}}{\overset{CH_3}{|}}{Si}-Cl + MgBrCl \quad a)$$

(V)

$$2C_{10}H_7MgBr + (CH_3)_2SiCl_2 \rightarrow (C_{10}H_7)_2Si(CH_3)_2 + 2MgBrCl \quad b)$$

(IX)

(1)

$$2C_{10}H_7MgBr + CH_3SiCl_3 \rightarrow (C_{10}H_7)_2\underset{\underset{CH_3}{|}}{SiCl} + 2MgBrCl \quad (2)$$

(VI)

In the preparation of (V) there was a byproduct (IX), which has not been described in the literature.

The preparation of (VI), (VII), and (VIII) by reaction of the corresponding halosilanes with 1-naphthyllithium proceeded according to the scheme:

$$2C_{10}H_7Li + CH_3SiCl_3 \rightarrow CH_3-\underset{\underset{Cl}{|}}{Si}-(C_{10}H_7)_2 + 2LiCl$$

(VI)

$$2C_{10}H_7Li + C_2H_5SiCl_3 \rightarrow C_2H_5\underset{\underset{Cl}{|}}{Si}-(C_{10}H_7)_2 + 2LiCl$$

(VII)

$$nC_{10}H_7Li + SiCl_4 \rightarrow \underset{(X)}{C_{10}H_7SiCl_3} + LiCl$$

$$\rightarrow \underset{(XI)}{(C_{10}H_7)_2SiCl_2} + 2LiCl$$

$$\rightarrow (C_{10}H_7)_3SiCl + 3LiCl$$

(VIII)

The general formula of the compounds required for the synthesis of the desired silanols is $(C_{10}H_7)_nR_{3-n}SiCl$, in which R = CH_3 or C_2H_5, and n = 1, 2, or 3. The byproducts (IX) and (XI) were isolated and characterized. The passage from halosilanes to the corresponding silanols can be effected by several methods:

$$R_3SiCl + H_2O + (alkali) \rightarrow R_3SiOH + HCl\,(MCl)\ [6], \quad (1)$$

in which R is alkyl or aryl and M is a metal;

$$2R_3SiCl + 3NH_3 \rightarrow R_3SiNHSiR_3 + 2NH_4Cl \quad a$$

$$R_3SiNHSiR_3 + 2H_2O + HCl \rightarrow 2R_3SiOH + NH_4Cl \quad b \quad [7-10] \quad (2)$$

$$2R_3SiCl + H_2O \rightarrow R_3SiOSiR_3 + 2HCl \quad a \quad [11]$$
$$R_3SiOSiR_3 + 3KOH \rightarrow 2R_3SiOK + KOH \cdot H_2O \quad b \quad [11] \qquad (3)$$

$$R_3SiOK + H_2O + CH_3COOH \rightarrow R_3SiOH + CH_3COOK \quad c \quad [12]$$

The first method, which is the simplest, is not suitable for the preparation of many silanols owing to the formation of condensation products (disiloxanes). For example, the following could not be prepared by this method: $(CH_3)_3SiOH$ [7,8]; $(CH_3)_2C_2H_5SiOH$ [9,10]; $CH_3(C_2H_5)_2SiOH$ [9,10]; $(CH_3)_2C_6H_5SiOH$ [3,12]; these were prepared by the second method, via the corresponding disilylamines. Unlike the above silanols, those which we now describe, (I), (II), (III), and (IV), were prepared by direct hydrolysis of the corresponding halosilanes in an ether medium. The fact that these naphthylsilanols can be prepared in this way indicates that they have considerable stability.

EXPERIMENTAL

Preparation of Chlorodimethyl-1-naphthylsilane and of Dimethyldi-1-naphthylsilane. The synthesis of chlorodimethyl-1-naphthylsilane was carried out in two stages. In the first stage 1-naphthylmagnesium bromide was prepared by the Grignard reaction from 52 g of magnesium and 316 g of 1-bromonaphthalene in 670 ml of ether by the usual method (in a flask fitted with reflux condenser, dropping funnel, thermometer, mechanical stirrer, and a tube for passage of dry nitrogen).

TABLE 1

Fraction	B.p. (°C at 3-4 mm)	Amount (g)	Notes
I	123—128	77.1	After removal of ether and before Fraction I, 18 g of naphthalene was distilled over
II	128—135	50.8	Liquid
III	145—210	3.6	Mixture of liquid and crystals
IV	210—215	23.9	Crystals
Residue		4	Solid resin

In the second stage the ethereal Grignard reagent was boiled gently and a solution of 240 g of dichlorodimethylsilane in 200 ml of dry ether was added from a dropping funnel over a period of two hours. The mixture was then stirred further for about three hours. When the mixture was cold, the precipitate was separated and the filtrate was vacuum-fractionated (Table 1).

TABLE 2

Fraction	B.p.(°C at 2.5-3 mm)	Amount (g)	d_4^{20}	n_D^{20}
I	121—123	37.3	1.1906	1.5957
II	123—124*	76.1	1.1910	1.5960
III	124—127*	12.95	1.1913	1.5964
IV	127—135*	0.53		

Fractions I and II were mixtures of chlorodimethyl-1-naphthylsilane and bromodimethyl-1-naphthylsilane. They were refractionated (Table 2).

Analysis of Fraction I

Found %: C 65.00; 64.96; H 5.82; 5.88; Si 12.67; 12.52; Cl 17.41; 17.13 $(CH_3)_2SiClC_{10}H_7$. Calculated %: C 65.31; H 5.94; Si 12.72; Cl 16.10

Analysis of Fraction II

Found %: C 62.76; 62.82; H 5.72; 5.72; Si 11.89; 12; Cl 19.21; 19.05 $(CH_3)_2SiClC_{10}H_7$. Calculated %: C 65.31; H 5.94; Si 12.72; Cl 16.10 $(CH_3)_2SiBrC_{10}H_7$. Calculated %: C 54.37; H 4.94; Si 10.58; Br 30.14

* There is some $(CH_3)_2C_{10}H_7SiBr$. impurity.

The results show that only Fraction I, b.p. 121-123° (2.5-3 mm) was pure and corresponded to chlorodimethyl-1-naphthylsilane in composition. The fractions of b.p. 123-124° (2.5-3 mm) and 127-135° (2.5-3 mm) were mixtures of chlorodimethyl-1-naphthylsilane and bromodimethyl-1-naphthylsilane.

The fraction of b.p. 145-210° (3-4 mm), amounting to 3.6 g, was a mixture of chlorodimethyl-1-naphthylsilane, bromodimethyl-1-naphthylsilane, and dimethyldi-1-naphthylsilane.

The fraction of b.p. 210-215° (3-4 mm) was recrystallized twice from hot heptane and had the following constants: m. p. 131°; found M 309, 5; 317.6; calculated M 312.44.

Found %: C 84.91; 84.90; H 6.57; Si 9.08; 8.98 $(CH_3)_2Si(C_{10}H_7)_2$. Calculated %: C 84.65; H 6.46; Si 8.99

These results show that the substance obtained corresponded to dimethyldi-1-naphthylsilane. Dimethyldi-1-naphthylsilane is a crystalline substance, soluble in benzene and hot heptane, insoluble in water, sparingly soluble at ordinary temperature in lower hydrocarbons (isopentane, heptane).

Preparation of Dimethyl-1-naphthylsilanol. A mixture of 30 ml of ether, 15 ml of water, and 1.52 g of chlorodimethyl-1-naphthylsilane was prepared in a flask fitted with stirrer and was titrated with 0.5 N NaOH in presence of phenolphthalein. The ether layer was separated, ether was distilled off under reduced pressure, and the crystalline residue was crystallized twice from heptane. The product, amounting to 0.92 g (60%), had m.p. 82-82.5°; found M 192.3; 201.4; calculated for $C_{12}H_{14}OSi$ M 202.29.

Found %: C 71.36; 71.43; H 6.95; 83; Si 13.90; 13.91 $(CH_3)_2C_{10}H_7SiOH$. Calculated %: C 71.24; H 6.97; Si 13.87

The analytical results correspond to dimethyl-1-naphthylsilanol. Dimethyl-1-naphthylsilanol crystallizes in prisms from heptane. It is sparingly soluble in water, but readily soluble in ether.

Preparation of Methyldi-1-naphthylsilanol. a) Synthesis of chloromethyldi-1-naphthylsilane. Chloromethyldi-1-naphthylsilane was prepared from 1-naphthylmagnesium bromide and trichloromethylsilane in 25-30% yield and from 1-naphthyllithium and trichloromethylsilane in 23% yield [14]; m. p. 130-132°. In addition, dichloromethyl-1-naphthylsilane was obtained, in 30-40% yield in the first case and in 40-45% yield in the second.

b) Hydrolysis of chloromethyldi-1-naphthylsilane. A mixture of 20 ml of water, 50 ml of ether, and 4.17 g of chloromethyldi-1-naphthylsilane was prepared in a flask fitted with stirrer, and with constant stirring 0.1 N NaOH was added until there was a stable color in presence of phenolphthalein. The aqueous layer was then separated and washed with ether. The ether extracts were combined and washed with water. Ether and traces of moisture were driven off under reduced pressure (at first with a water pump and then with an oil pump). The residue (3.38 g) was crystallized twice from heptane; the product had m.p. 113-114°; found M 309.8; 317.6; calculated M 314.41.

Found %: C 80.72; 80.73; H 6.03; 6.20; Si 8.65; 8.28; O 4.60; 4.82 $CH_3(C_{10}H_7)_2SiOH$. Calculated %: C 80.21; H 5.77; Si 8.92; O 5.08.

On the basis of the method of preparation and the analytical results it follows that the substance isolated was methyldi-1-naphthylsilanol; it formed crystals, readily soluble in benzene, appreciably soluble in hot heptane, sparingly soluble in the cold in lower aliphatic hydrocarbons, and insoluble in water.

Preparation of Ethyldi-1-naphthylsilanol. a) Synthesis of chloroethyldi-1-naphthylsilane. Chloroethyldi-1-napthylsilane was prepared by a method described previously [4]; m. p. 94°.

Found %: C 75.86; 75.34; H 5.69; 5.65; Cl 11.14; Si 7.54; 7.94 $CH_3(C_{10}H_7)_2SiCl$. Calculated %: C 76.15; H 5.52; Cl 10.22; Si 8.09

b) Hydrolysis of chloroethyldi-1-naphthylsilane. The hydrolysis conditions were the same as those used for chloromethyldi-1-naphthylsilane, the only difference being the longer period of treatment (2-3 hours). After removal of ether the reaction product remained as a highly viscous substance, which crystallized very slowly from heptane (12 days); m.p. 98-103°; found M 312.6; 321.8; calculated M 328.44

Found %: C 80.55; 80.65; H 6.31; 6.39; Si 8.15; 8.28; O 4.99; 4.73 $C_2H_5(C_{10}H_7)_2SiOH$. Calculated %: C 80.41; H 6.14; Si 8.54; O 4.87

On the basis of these results the product was ethyldi-1-naphthylsilanol, a crystalline substance, soluble in ether, benzene, and hot heptane, sparingly soluble in cold lower aliphatic hydrocarbons, and almost insoluble in water.

Preparation of Dichlorodi-1-naphthylsilane and of Chlorotri-1-naphthylsilane. Dry benzene (250 ml) was introduced into a flask fitted with reflux condenser, dropping funnel, thermometer, and mechanical stirrer, air was displaced by nitrogen (all operations with organolithium compounds were carried out in an atmosphere of nitrogen), a mixture of 162 g of 1-naphthyllithium and 200 ml of benzene was added, and the contents of the flask were stirred while dropwise addition was made of 95.5 g of silicon tetrachloride over two hours at 18-20°. The reaction temperature was then raised to 50-60° over a period of one hour, and heating was continued for two hours further. The reaction mixture was then cooled, and the crystalline precipitate was filtered off and washed with benzene. Benzene was vacuum-distilled from the filtrate (100-20 mm), and the residue was washed twice with isopentane and crystallized from heptane and benzene. In this way two substances were isolated.

The first substance had b.p. 230-235° (3 mm); m.p. 151-152°; found M 336.0; 348; calculated M 353.28.

Found %: C 68.23; 68.27; H 4.03; 3.98; Si 8.28; 8.18; Cl 19.58 $(C_{10}H_7)_2SiCl_2$. Calculated %: C 67.98; H 3.99; Si 7.93; Cl 20.06.

According to these results this substance was dichlorodi-1-naphthylsilane. It was readily soluble in benzene and hot heptane, but sparingly soluble in isopentane.

The second substance had b.p. 309-313° (2-3 mm); m.p. 210°; found M 437.6; 456; calculated M 444.99.

Found %: C 81.69; 81.69; H 4.95; 4.92; Si 6.19; 5.68; Cl 7.84; 7.83 $(C_{10}H_7)_3SiCl$. Calculated %: C 80.97; H 4.76; Si 6.30; Cl 7.97

The substance was chlorotri-1-naphthylsilane. It was soluble in benzene: poorly in the cold, but readily hot. It was sparingly soluble in aliphatic hydrocarbons.

Preparation of Tri-1-naphthylsilanol. Tri-1-naphthylsilanol was prepared from chlorotri-1-naphthylsilane by hydrolysis with aqueous alkali in an ether medium by the method described above for the preparation of methyldi-1-naphthylsilanol, but in this case it was found that an 8- to 10 hour treatment was required. When ether was distilled from the ether extract, crystals were formed which were recrystallized from benzene, washed with isopentane, and vacuum-dried (1-2 mm); m.p. 183-189° ; found M 392.4; 430.3; calculated M 426.54.

Found %: C 82.79; 83.05; H 5.19; 5.09; Si 6.04; 5.95 $(C_{10}H_7)_3SiOH$. Calculated %: C 84.45; H 5.20; Si 6.58

On the basis of the method of preparation and the analytical data, the substance was tri-1-naphthylsilanol. The substance crystallized from benzene in prisms, readily soluble in ether and hot benzene, sparingly soluble in lower aliphatic hydrocarbons, and almost insoluble in water.

SUMMARY

1. The following compounds are described for the first time: dimethyl-1-naphthyl-, methyldi-1-naphthyl-, ethyldi-1-naphthyl- silanols and dimethyldi-1-naphthylsilane.

2. The conditions were found for the hydrolysis of chlorodimethyl-1-naphthyl-, chloromethyldi-1-naphthyl-, chloroethyldi-1-naphthyl-, and chlorotri-1-napthyl-silanes with formation of the corresponding silanols in good yield.

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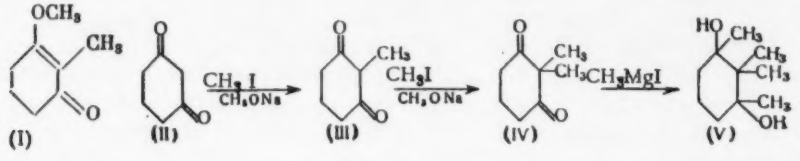
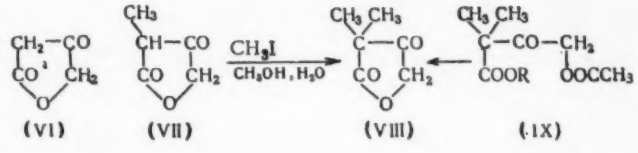
EFFECT OF SOLVENTS ON THE REACTIVITY OF CARBONYL COMPOUNDS IN MICHAEL AND C-ALKYLATION REACTIONS

I. N. Nazarov and S. I. Zavyalov

It is known that 1,3-cyclohexanedione derivatives, although having a high tendency to undergo enolization, can nevertheless be C-alkylated under suitable conditions. For example, when methylated with methyl iodide in polar solvents (aqueous acetone, methanol), 1, 3-cyclohexanedione itself (II) [1, 2] gives a 50% yield of 2-methyl-1,3-cyclohexanedione (III), which when methylated further under these conditions, in spite of statements in the literature [3], gives not the enol ether (I), but 2,2-dimethyl-1,3-cyclohexanedione (IV) in 40% yield. This diketone has two reactive keto groups and gives the diol (V) when treated with excess of methylmagnesium iodide.

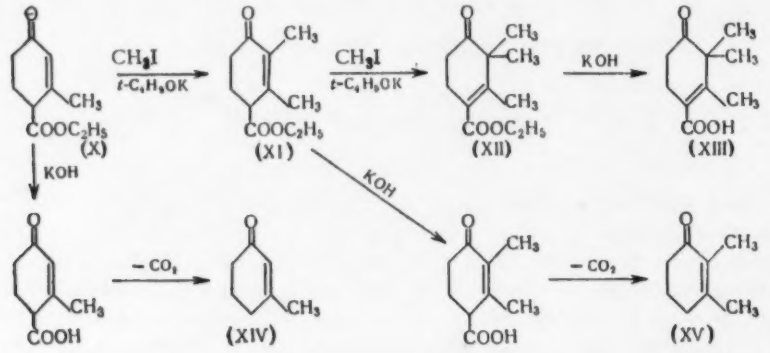


Alkyl derivatives of tetronic acid (2,4(3H,5H)-furandione) (VI), which are completely enolized in aqueous solutions [4], again undergo Michael and C-alkylation reactions only in strongly polar solvents. For example, 3-methyltetronic acid (VII) is C-methylated in boiling aqueous methanol, but is not methylated appreciably in boiling absolute methanol and tert-butyl alcohol [5]. The 3,3-dimethyltetronic acid (VIII) obtained by the direct methylation of 3-methyltetronic acid is identical with the cyclization product from 4-acetoxy-2,2-dimethylacetoacetic ester (IX) [6].

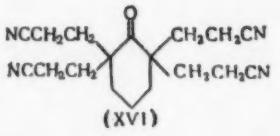


Methylation of the weakly enolized Hagemann's ester (ethyl 2-methyl-4-oxo-2-cyclohexene-1-carboxylate) (X) [7] proceeds extremely rapidly in tert-butyl alcohol at room temperature, and a high yield is obtained of ethyl 2,3-dimethyl-4-oxo-2-cyclohexene-1-carboxylate (XI), the structure of which was confirmed by hydrolysis and decarboxylation to 2,3-dimethyl-2-cyclohexen-1-one (XV). Further methylation of the ester (XI) in the tert-butyl alcohol also proceeds vigorously and results in the formation of a liquid reaction product, which when boiled with aqueous-methanolic potassium hydroxide and then with a mixture of hydrochloric and

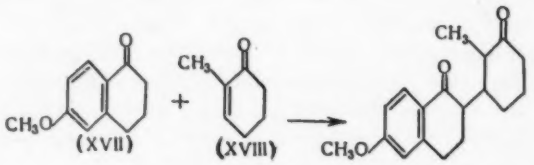
acetic acids gives crystalline 2,3,3-trimethyl-4-oxo-1-cyclohexene-1-carboxylic acid (XIII). The structure of this acid was confirmed by its inability to undergo decarboxylation under the usual conditions and by its conversion into a yellow 2,4-dinitrophenylhydrazone having an absorption maximum at 365 mμ (in methanol), which is characteristic for 2,4-dinitrophenylhydrazones of unsaturated ketones.



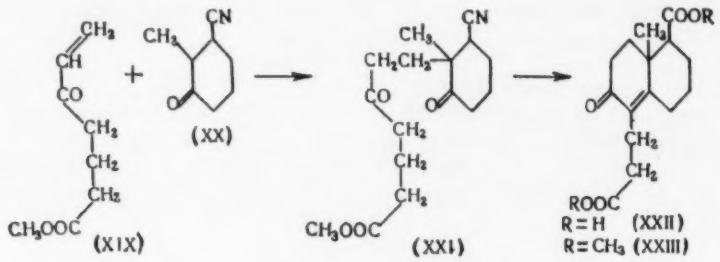
Numerous examples show that the mobility of hydrogen in keto-enol compounds in nucleophilic reactions is dependent on many factors, including the nature of the reaction medium. It has been noted earlier [5, 8] that 1,3-cyclohexanedione derivatives do not undergo the Michael reaction so readily as other weakly enolized carbonyl compounds. It was noted also [5, 8] that Michael and C-alkylation reactions with 1,3-cyclohexanedione derivatives proceed most satisfactorily in polar solvents (alcohol, aqueous alcohol, aqueous dioxane). However, in the case of weakly acid keto-enols (cyclohexanone, etc.) which form metal derivatives that are unstable in aqueous solutions, these reactions often proceed better in nonaqueous solvents, e.g., tert-butyl alcohol. In an aqueous medium, which is the most satisfactory for the C-alkylation of 1,3-cyclohexanedione, cyclohexanone is not alkylated appreciably. On the other hand, in tert-butyl alcohol cyclohexanone and its derivatives undergo Michael and C-alkylation reactions and react considerably more rapidly than 1,3-cyclohexanedione derivatives [5, 9]. In tert-butyl alcohol in presence of potassium tert-butoxide the weakly enolized [10] cyclohexanone reacts vigorously with acrylonitrile with almost instantaneous formation of the tetrakiscyanoethyl derivative (XVI) in 64% yield. Under the same conditions, but with an addition of water, such exhaustive cyanoethylation does not occur to an appreciable extent and much of the cyclohexanone is recovered unchanged.



3,4-Dihydro-6-methoxy-1-(2H)-naphthalenone (XVII) condenses satisfactorily with 2-methyl-2-cyclohexen-1-one (XVIII) only in dry tert-butyl alcohol [11].



We found that the Michael condensation of methyl 5-oxo-6-heptenoate (XIX) with 2-methyl-3-oxocyclohexanercarbonitrile (XX) again proceeds rapidly in dry tert-butyl alcohol. The normal reaction product (XXI) was not isolated in the pure state but was converted by treatment with a boiling mixture of hydrochloric and acetic acids into the bicyclic dicarboxylic acid (XXII), which was purified via the corresponding dimethyl ester (XIII).



In an aqueous-alcohol medium the methylation of Hagemann's ester proceeds much less vigorously than in tert-butyl alcohol and is accompanied by hydrolysis and decarboxylation with formation of 3-methyl-1-cyclohexen-1-one (XIV).

EXPERIMENTAL

Methylation of 2-Methyl-1,3-cyclohexanedione. A mixture of 3 g of methyl iodide and the sodium derivative of 2-methyl-1,3-cyclohexanedione prepared from 0.4 g of sodium, 10 ml of absolute methanol, and 2.5 g of 2-methyl-1,3-cyclohexanedione (III) (m.p. 208-209°) [1] was refluxed for two hours. Solvent was removed, and the residue was treated with water and extracted with chloroform. The product, amounting to 1.3 g (46%), was 2,2-dimethyl-1,3-cyclohexanedione (IV), b.p. 115-118° (25 mm) and m.p. 38-39° [8].

Reaction of 2,2-Dimethyl-1,3-cyclohexanedione with Methylmagnesium Iodide. A solution of 4.2 g of 2,2-dimethyl-1,3-cyclohexanedione in 20 ml of ether was added to a stirred ice-cooled Grignard reagent prepared from 3 g of magnesium and 22 g of methyl iodide in 100 ml of ether. The mixture was set aside for 12 hours at room temperature and then treated with ice and hydrochloric acid. The ether layer gave 3 g (58%) of the diol (V), m.p. 124-125° (from isooctane).

Found %: C 69.67; 69.79; H 11.74; 11.80 $C_{10}H_{20}O_2$. Calculated %: C 69.70; H 11.60

Methylation of 3-Methyltetronic Acid. A mixture of 2.4 g of potassium hydroxide, 4.6 g of 3-methyltetronic acid (VII) (m.p. 189-190°) [12], 10 ml of water, 30 ml of methanol, and 6 g of methyl iodide was refluxed for four hours. The solution was cooled, diluted with water, and extracted with chloroform. The product, amounting to 1.4 g (27%), was 3,3-dimethyltetronic acid (VIII), b.p. 112-114° (20 mm) and n_D^{20} 1.4550. Its phenylhydrazone melted at 129-130° (from aqueous methanol) and its oxime at 133-134° (from water). The literature [6] gives 131° and 134° respectively for the phenylhydrazone and oxime of 3,3-dimethyltetronic acid.

Methylation of Hagemann's Ester. 1. Methyl iodide (3 g) was added to a stirred suspension of a potassium derivative prepared from 0.8 g of potassium, 15 ml of butyl alcohol, and 3.6 g of Hagemann's ester (b.p. 113-118° (1 mm) and n_D^{20} 1.4880) [7]. Reaction was so vigorous that the mixture came to the boil in a few seconds. After one hour solvent was removed under reduced pressure and the residue was treated with water and extracted with ether. The product, amounting to 3 g (77%), was ethyl 2,3-dimethyl-4-oxo-2-cyclohexene-1-carboxylate (XI) [13], b.p. 105-107° (1 mm) and n_D^{20} 1.4854. The 2,4-dinitrophenylhydrazone melted at 123-125° (from alcohol).

Found %: N 15.21; 15.32 $C_{17}H_{20}O_6N_4$. Calculated %: N 14.9

The methylation product (XI) was almost insoluble in alkali in the cold. When boiled with aqueous-methanolic alkali it gave 2,3-dimethyl-2-cyclohexen-1-one (XV), b.p. 107-109° (28 mm) and n_D^{20} 1.4935 [13] (its 2,4-dinitrophenylhydrazone melted at 191-193°).

2. To a solution of 1.2 g of potassium hydroxide in 5 ml of water, which was cooled with ice and stirred, 3.6 g of Hagemann's ester in 10 ml of alcohol, and then 3 g of methyl iodide, were added. After a few minutes the temperature of the solution rose to 45°. The mixture was allowed to stand at room temperature for two hours and was then extracted with ether. Fractionation gave 1.2 g of 3-methyl-2-cyclohexen-1-one (XIV), b.p. 98-101° (23 mm) and n_D^{20} 1.4862, the 2,4-dinitrophenylhydrazone of which melted at 180-182° [14]. In addition, 1 g of ethyl 2,3-dimethyl-4-oxo-2-cyclohexene-1-carboxylate (XI), b.p. 108-112° (1 mm) and n_D^{20} 1.4860, was obtained; its 2,4-dinitrophenylhydrazone had m.p. 122-124°, undepressed by admixture of the dinitrophenylhydrazone obtained previously (above).

Methylation of Ethyl 2,3-Dimethyl-4-oxo-2-cyclohexene-1-carboxylate. Methyl iodide (6 g) was added in one portion to a suspension of the potassium derivative obtained from 1.2 g of potassium, 20 ml of tert-butyl alcohol, and 6 g of ethyl 2,3-dimethyl-4-oxo-2-cyclohexene-1-carboxylate (XI). The reaction mixture came to the boil in a few seconds. The mixture was allowed to stand for one hour at room temperature, treated with water, and extracted with ether. The product (5 g) was the keto ester (XII), b.p. 104-106° (1 mm) and n_D^{20} 1.4853.

Found %: C 67.92; 67.98; H 8.37; 8.32 $C_{12}H_{18}O_3$. Calculated %: C 68.6; H 8.6

Hydrolysis of the Keto Ester (XII). A mixture of solutions of 5 g of the above-described keto ester (XII) in 30 ml of methanol and of 3 g of potassium hydroxide in 10 ml of water was refluxed for three hours. The cooled solution was acidified with concentrated hydrochloric acid and extracted with ether. After removal of solvent the oily residue was boiled with 3 ml of water, 5 ml of concentrated hydrochloric acid, and 30 ml of acetic acid for one hour. Solvents were distilled off under reduced pressure, and the residue was treated with excess of sodium carbonate and extracted with ether. The alkaline solution, after acidification and extraction with ether, gave 2 g of 2,3,3-trimethyl-4-oxo-1-cyclohexene-1-carboxylic acid (XIII), m.p. 114-115° (from heptane).

Found %: C 65.79; 66.00; H 7.80; 7.75 $C_{10}H_{14}O_3$. Calculated : C 65.9; H 7.7.

Titration equivalent: found 180; 179 calculated for $C_{10}H_{14}O_3$ 182

The yellow 2,4-dinitrophenylhydrazone of the keto acid (XIII) melted at 191-193° (from methanol); λ_{max} 365 mμ (in methanol).

Found %: N 15.83; 15.88 $C_{16}H_{18}O_6N_4$. Calculated %: N 15.5

Reaction of Methyl 5-oxo-6-heptenoate with 2-Methyl-3-oxocyclohexanecarbonitrile. A solution of potassium tert-butoxide was prepared from 0.2 g of potassium and 7 ml of dry tert-butyl alcohol and was stirred while 15 g of 2-methyl-3-oxocyclohexanecarbonitrile (XX), m.p. 57-58° [15], in 6 ml of dry tert-butyl alcohol was added; a mixture of 15 g of the keto nitrile (XX) and 11 g of methyl 5-oxo-6-heptenoate (XIX) (b.p. 70-71° (2 mm) and n_D^{20} 1.4481)[8] was then added. The mixture was allowed to stand for three hours at room temperature and was then treated with excess of dilute hydrochloric acid and extracted with ether. The reaction product (XXI) was freed from admixed unchanged 2-methyl-3-oxocyclohexanecarbonitrile by distilling the latter off at 1 mm (bath temperature 150-155°). The residue (19 g) was boiled for 20 hours with a mixture of 50 g of concentrated hydrochloric acid and 150 ml of acetic acid. When the cooled solution was diluted with water there separated a viscous oil which crystallized when rubbed with a mixture of ether and acetone. The crude acid so obtained (8 g) was treated without further purification with 3% ethereal diazomethane, which gave 4.5 g of the dimethyl ester (XXIII), b.p. 182-185° (1 mm) and n_D^{20} 1.5220.

Found %: C 66.24; 66.12; H 7.96; 8.13 $C_{17}H_{24}O_5$. Calculated %: C 66.20; H 7.80

Hydrolysis of the Dimethyl Ester (XXIII). A mixture of 0.2 g of the above-described dimethyl ester (XXIII) and 20 ml of 1 : 1 hydrochloric acid was boiled for six hours. Hydrochloric acid was removed under reduced pressure, and 5 ml of water was added to the residue. The product (0.1 g) was the dicarboxylic acid (XXII), m. p. 201-203° (from aqueous dioxane).

Found %: C 64.22; 64. 06; H 7.29; 7.19 $C_{15}H_{20}O_5$. Calculated %: C 64.3; H 7.2

Titration equivalent: found 142; 143 calculated for $C_{13}H_{18}O(COOH)_2$ 140

Cyanoethylation of Cyclohexanone. Cyclohexanone (5 g) was added to a solution of 0.1 g of potassium in 12 ml of dry tert-butyl alcohol, and the solution was stirred while 11 g of acrylonitrile was added over a period of ten minutes. There was considerable evolution of heat, and the reaction temperature was maintained at 40-50° by external cooling. Treatment with dilute hydrochloric acid gave a precipitate, which was filtered off and washed with methanol. The product, amounting to 10.5 g (64%), was the tetrakiscyanoethyl derivative (XVI), m. p. 160-162° (from alcohol and acetone) [16].

SUMMARY

1. When boiled in methanol solution with methyl iodide, the sodium derivative of 2-methyl-1,3-cyclohexanedione (III) gives 2,2-dimethyl-1,3-cyclohexanedione (IV) in 40% yield.

2. When boiled for four hours with methyl iodide in aqueous methanol, the potassium derivative of 3-methyltetronic acid (VII) gives 3,3-dimethyltetronic acid (VIII) in 27% yield.

3. The potassium derivative of Hagemann's ester (X) reacts vigorously with methyl iodide in dry tert-butyl alcohol at room temperature with formation of ethyl 2,3-dimethyl-4-oxo-2-cyclohexene-1-carboxylate (XI) in 77% yield. Further methylation of Hagemann's ester under the same conditions gives the dimethyl derivative (XII), hydrolysis of which gives 2,3,3-trimethyl-4-oxo-1-cyclohexene-1-carboxylic acid (XIII).

4. Reaction of methyl 5-oxo-6-heptenoate (XIX) with 2-methyl-3-oxocyclohexanecarbonitrile (XX) in tert-butyl alcohol in presence of potassium tert-butoxide, followed by hydrolysis and cyclization of the reaction product (XXI), gives the bicyclic dicarboxylic acid (XXII).

5. Unlike the strongly enolized (acidic) derivatives of 1,3-cyclohexanedione and tetronic acid, which undergo Michael and C-alkylation reactions more readily in aqueous solvents, neutral carbonyl compounds such as cyclohexanone generally react more readily in nonaqueous solvents such as dry tert-butyl alcohol.

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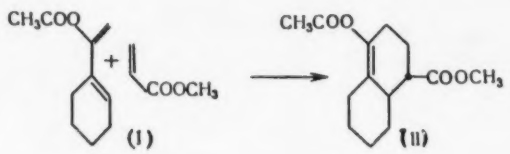
STEREOCHEMISTRY OF CYCLIC COMPOUNDS

COMMUNICATION 17. CONDENSATION OF 1-(1-ACETOXYVINYL) CYCLOHEXENE WITH MALEIC ANHYDRIDE

I. N. Nazarov, V. F. Kucherov, and V. M. Andreev

As was shown previously [1], the use of 1-(1-acetoxyvinyl)cyclohexene (I) in diene-condensation reactions opens up a new way to the synthesis of polycyclic ketones containing the trans-octahydro-1(2H)-naphthalenone system. The steric characteristic of the condensation of such a diene with methyl acrylate consists in the preferential formation of the antiisomer (II), the configuration of which corresponds to orientation of the reactants in violation of the rule of "accumulation of unsaturation" because of the electronegative enol-acetate group of the diene [2].



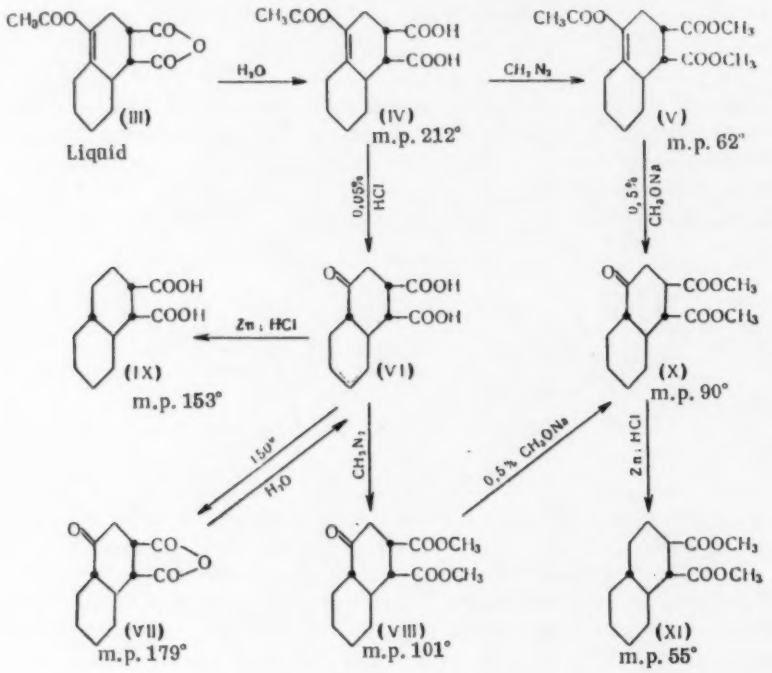
These circumstances lend great interest to the use of 1-(1-acetoxyvinyl)cyclohexene for the stereospecific synthesis of polycyclic compounds, and advantage was taken of them in our preparation [3] of some geometric isomers of decahydro-1,2-naphthalenedicarboxylic acid and in the proof of the configurations of these compounds. It was found that boiling of 1-(1-acetoxyvinyl)cyclohexene (I) with maleic anhydride in benzene solution gave the anti-cis anhydride (III), in 80% yield; hydrolysis of this with water gave the anti-cis dicarboxylic acid (IV), which gave the crystalline anti-cis diester (V) with diazomethane. Under mild conditions (0°, 25 days) this condensation was slow, but the only product was again the anti-cis anhydride (III). All these products, which contained an enol-acetate group, were very sensitive to the action of alkalis and readily resinified even under weakly alkaline conditions.

With the object of obtaining decahydro-4-oxo-1,2-naphthalenedicarboxylic acid and proving the anti-cis configuration of the adduct (III), we made a detailed study of the conditions for the enol-acetate group in the acetoxy acid (IV) and its ester (V).

Hydrolysis of the acetoxy acid (IV) proceeded most satisfactorily when it was boiled for a short time with 0.05% hydrochloric acid, and under these conditions a 60% yield was obtained of trans-anti-cis-decahydro-4-oxo-1,2-naphthalenedicarboxylic acid (VI) in the form of its monohydrate, m.p. 121-123°. Attempts to obtain the anhydrous acid (VI) by careful heating of its monohydrate in a vacuum resulted in partial formation of the anhydride, and heating of the keto acid (VI) at 150° for a short time was sufficient to give pure trans-anti-cis keto anhydride (VII) in good yield. Hydrolysis of this anhydride with water gave a quantitative yield of the original keto acid (VI), which gave the corresponding trans-anti-cis keto diester (VIII) with diazomethane.

Trans-anti-cis- decahydro-4-oxo-1,2-naphthalenedicarboxylic acid (VI) has a cis arrangement of hydrogen atoms at C-1, C-2, and C-4a, and Clemmensen reduction converts it into trans-anti-cis-decahydro-1,2-naphthalenedicarboxylic acid (IX), the configuration of which we established previously [3] on the basis of the

steric regularities observed in the hydrogenation of 1,2,3,5,6,7,8,8a-octahydro-1,2-naphthalenedicarboxylic acids [4]. Confirmation of these results was found also in a study of the hydrolysis of the anti-cis acetoxy diester (V). In this case boiling with 0.5% sodium methoxide solution resulted in hydrolysis of the acetic ester grouping and simultaneous isomerization at the 2-methoxycarbonyl group with formation of the trans-anti-trans keto diester (X), which is formed also in the isomerization of pure trans-anti-cis keto diester (VIII) with the aid of sodium methoxide. Clemmensen reduction of the trans-anti-trans keto diester (X) gave crystalline trans-anti-trans-decahydro-1,2-naphthalenedicarboxylic diester (XI), which was again found to be identical with the preparation obtained previously [3]. Hence, by the above-described independent and stereospecific syntheses, complete confirmation was obtained of the configurations of all six previously prepared [3] stereoisomers of decahydro-1,2-naphthalenedicarboxylic acid. This implies confirmation also of the correctness of the steric laws for hydrogenation, isomerization, and thermal transformation on which these configurations were based.



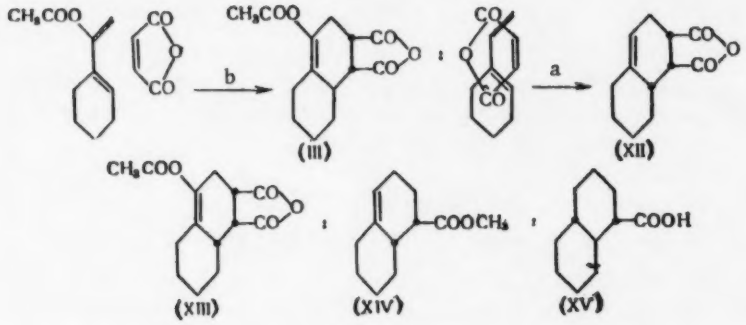
At the same time these results prove rigorously that the condensation of 1-(1-acetoxyvinyl)cyclohexene (I) with maleic anhydride gives the adduct (III), which has an anti-cis configuration, whereas in the condensation of 1-vinylcyclohexene with maleic anhydride the greatly predominating adduct is, as shown previously [4], the compound (XII) of syn-cis configuration. It appears that the corresponding adduct (XIII) for condensation of the diene (I) with maleic anhydride is not formed at all.

In this way we have established for the first time the very interesting fact of the strong effect of a substituent in a diene on steric orientation in the diene condensation. Reaction of 1-vinylcyclohexene with maleic anhydride proceeds preferentially in accordance with scheme "a", whereas, owing to the influence of the electrogenative acetoxy group, 1-(1-acetoxyvinyl)cyclohexene condenses with maleic anhydride exclusively in accordance with scheme "b", i.e., in the direction opposite to that required by the "accumulation of unsaturation" rule.

Similar stereochemical regularities were established also for the condensation of 1-vinyl- and 1-(1-acetoxyvinyl)-cyclohexenes with acrylic ester.* In the first case the adduct (XIV) of syn configuration was formed preferentially

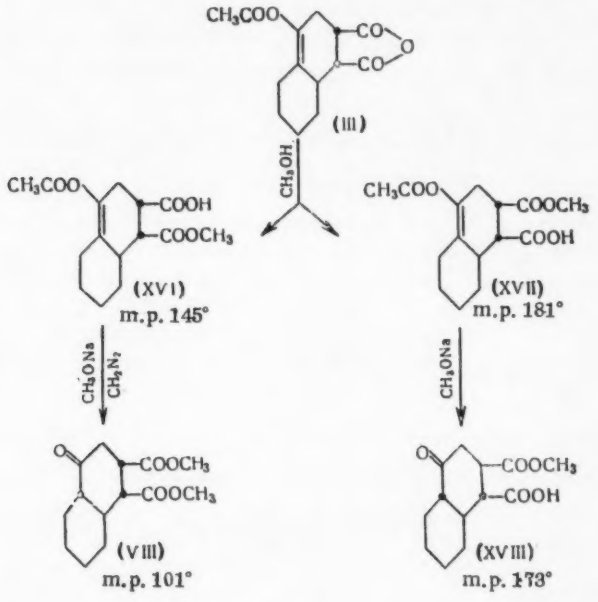
* Simultaneously with us, other authors published preliminary data on the condensation of 1-(1-acetoxyvinyl) cyclohexene with various dienophiles, but the configurations of the resulting adducts were not proved [6].

[5], whereas in the second case, as indicated above, the adduct (II) of anti configuration was formed [2], the



structure of this being proved by its conversion into the known trans-anti-decahydro-1-naphthoic acid (XV). However, in their stereochemistry the diene condensations of 1-(1-acetoxyvinyl)cyclohexene with maleic anhydride and with methyl acrylate differ substantially, for with maleic anhydride the reaction proceeds essentially according to scheme "b", whereas with methyl acrylate this direction of condensation is merely the predominating one.

In order to confirm the above-stated fact of the ready transisomerization at the 2-methoxycarbonyl group in the process of hydrolysis of the anti-cis acetoxy ester (V) with 0.5% sodium methoxide solution, we made a detailed study of the isomerization of the corresponding monoesters; for the preparation of these we used the reaction of anhydrides with methanol, which we have often used previously and which has been proved to lead to ester formation at the less screened 2-carboxyl. It was found that boiling of the anti-cis acetoxy anhydride (III) with methanol gave a mixture of isomeric anti-cis monoesters (XVI) and (XVII) with great predominance of the second, which was separated by fractional crystallization. When the monoester (XVII) was boiled with 0.5% sodium methoxide solution, it was isomerized in high yield to the trans-anti-trans keto monoester (XVIII), esterification of which gave the trans-anti-transketo diester (X), identical with the compound described above.



Unlike the monoester (XVII), the isomeric monoester (XVI) was found to be unable to undergo isomerization in presence of sodium methoxide, and by treatment with diazomethane it gave the trans-anti-cis keto diester (VIII) obtained previously (above). These results prove that the monoester (XVII) obtained as main reaction product has an esterified carboxyl group at C-2 and that it is only at this carbon that ready trans isomerization occurs in the case of the anti-cis acetoxy diester (V).

As can be readily seen, the monoester (XVIII) with a free carboxyl at C-1 may be of interest for the synthesis of stereoisomeric polycyclic ketones by the method of lengthening the carbon chain by the Arndt-Eistert reaction.

EXPERIMENTAL

Condensation of 1-(1-Acetoxyvinyl)cyclohexene (I) with Maleic Anhydride

a) A mixture of 20 g of 1-(1-acetoxyvinyl)cyclohexene (I), 11.8 g of maleic anhydride, and 80 ml of dry benzene was boiled for nine hours. Benzene was distilled off, and vacuum distillation of the residue gave 26.1 g (80%) of the anti-cis acetoxy anhydride (III) as a light-yellow viscous liquid, b.p. 214-215° (6 mm) [1].

b) A mixture of 5 g of the diene (I), 2.8 g of maleic anhydride, and 20 ml of dry benzene was set aside at 0° for 25 days. Benzene was distilled off, and vacuum distillation of the residue gave 5.1 g of the anti-cis acetoxy anhydride (III), b.p. 214-216° (6 mm).

The adducts obtained by the two methods were identical, since they gave the same anti-cis acetoxy acid (IV), m. p. 211-212°, when hydrolyzed with water.

anti-cis-4-Acetoxy-1,2,3,5,6,7,8,8a-octahydro-1,2-Naphthalenedicarboxylic Acid (IV)

A mixture of 9 g of the anti-cis acetoxy anhydride (III) and 40 ml of water was boiled for ten minutes, and the crystals that separated on cooling were filtered off, washed with a little water, and dried in a vacuum desiccator. The product (8.1 g) was the anti-cis acetoxy acid (IV), m.p. 207-210°, raised to a constant value of 211-212° (with decomposition) by crystallization from 50% acetic acid.

Found %: C 59.45; 59.31; H 6.69; 6.72 $C_{14}H_{18}O_6$. Calculated %: C 59.56; H 6.43

anti-cis Acetoxy Diester (V)

A suspension of 4.1 g of the above anti-cis acetoxy acid (IV) was treated in ether with diazomethane. Ether was distilled off, and vacuum distillation of the residue gave 4.2 g of the anti-cis acetoxy diester (V), a colorless viscous substance, b.p. 184-185° (5 mm), which gradually solidified with standing. After crystallization from a 1 : 2 mixture of diethyl ether and petroleum ether, the anti-cis acetoxy diester (V) was isolated as fine needles, m.p. 60.5-62°.

Found %: C 61.80; 61.77; H 7.13; 7.22. $C_{16}H_{22}O_6$. Calculated %: C 61.92; H 7.14

trans-anti-cis-Decahydro-4-oxo-1,2-naphthalenedicarboxylic Acid (VI)

A mixture of 4 g of the anti-cis acetoxy acid (IV) and 30 ml of 0.05% hydrochloric acid was boiled until solution was complete (45 minutes). The solution was filtered, evaporated down to one-third bulk, and cooled to room temperature. The product (3.4 g of crystals, m.p. 108-115°) was recrystallized from 16 ml of hot water. After one hour at room temperature the crystals were filtered off (2.3 g , m.p. 115-118°). The product was the hydrate of the trans-anti-cis keto acid (VI). After two crystallizations from water (both times from 10 ml of water with filtration after one hour) the pure hydrate of the trans-anti-cis keto acid (VI) melted at 121-123° (with decomposition).

Found %: C 56.0; 55.80; H 7.10; 7.05 $C_{12}H_{16}O_5 \cdot H_2O$. Calculated %: C 55.80; H 7.02

Found : M 255.7 (titration with NaOH) Calculated: M 258.3

When dried in a vacuum desiccator at 40-50°, the hydrate passed partially into the anhydride and formed an inhomogeneous polycrystalline mass.

trans-anti-cis Keto Anhydride (VII)

The monohydrate of the trans-anti-cis keto acid (VI) (0.8 g) was heated in a vacuum for one hour at 150°

and then treated with benzene. The crystalline reaction product was filtered off and amounted to 0.6 g. After two crystallizations from benzene containing a little acetone, the trans-anti-cis keto anhydride (VII) had a constant melting point of 178-179°.

Found %: C 64.84; 64.80; H 6.44; 6.35 $C_{12}H_{14}O_4$. Calculated %: C 64.85; H 6.30

When boiled with water this anhydride was converted quantitatively into the original acid (VI) in the form of its monohydrate, m.p. 121-123°.

trans-anti-cis Keto Diester (VIII)

A suspension of 0.4 g of the monohydrate of the trans-anti-cis keto acid (VI) in ether was treated with ethereal diazomethane, ether was distilled off, and the residue was heated at 100° for five minutes to remove crystallization water and then treated with petroleum ether. The product (0.3 g) was trans-anti-cis keto ester (VIII). m.p. 90-95°, raised to a constant value of 100-101° by one crystallization from ether.

Found %: C 62.55; 62.67; H 7.60; 7.58 $C_{14}H_{20}O_5$. Calculated %: C 62.67; H 7.51

The 2,4-dinitrophenylhydrazone was prepared in the usual way and melted at 214-215° after crystallization from 1 : 1 alcohol-chloroform mixture.

Found %: N 12.54; 12.67 $C_{20}H_{24}O_8N_4$. Calculated %: N 12.49

Clemmensen Reduction of trans-anti-cis-Decahydro-4-oxo-1,2-naphthalenedicarboxylic Acid (VI)

A mixture of 1.65 g of amalgamated zinc, 1.5 ml of water, 3 ml of concentrated hydrochloric acid, and 1 g of the monohydrate of the trans-anti-cis keto acid (VI) was boiled for four hours, after which 2 ml of concentrated hydrochloric acid was added and the mixture boiled further for four hours. When the mixture was cooled, the crystalline reduction product separated and was filtered off and washed with water. The product (0.55 g) was trans-anti-cis-decahydro-1,2-naphthalenedicarboxylic acid (IX), which melted with decomposition at 152-153° after crystallization from aqueous acetone; there was no depression of melting point in admixture with a sample prepared previously [3].

trans-anti-trans Keto Diester (X)

a) The anti-cis acetoxy diester (V) (5.5 g) was added to a solution of 0.2 g of sodium in 40 ml of absolute methanol, the mixture was boiled for 3.5 hours and then acidified with acetic acid, and methanol was distilled off under reduced pressure. Water (10 ml) was added to the residue, and the mixture was extracted with ether. Ether was distilled off, and vacuum distillation of the reaction product gave 2.7 g of a viscous oil, b.p. 171-175° (4 mm). The product was dissolved in 5 ml of ether, and the solution was then diluted with 10 ml of petroleum ether. On the next day 1.1 g of the trans-anti-trans keto diester (X), m.p. 87-89°, had separated. The liquid residue was again boiled with a solution of 0.05 g of sodium in 10 ml of absolute methanol, and the above-described treatment gave a further 0.3 g of the keto diester (X), m.p. 86-88°. Crystallization from a little ether gave pure trans-anti-trans keto diester (X), melting constantly at 89-90°.

Found %: C 63.02; 63.04; H 7.45; 7.61 $C_{14}H_{20}O_5$. Calculated %: C 62.67; H 7.51

The 2,4-dinitrophenylhydrazone was prepared in the usual way and melted at 178-179° (from a mixture of alcohol and chloroform).

Found %: N 12.69; 12.79 $C_{20}H_{24}O_8N_4$. Calculated %: N 12.49

b) A mixture of 6.5 ml of a 0.5% solution of sodium methoxide in absolute methanol and 0.8 g of the trans-anti-cis keto diester (VIII) was boiled for 3.5 hours. The above-described treatment gave 0.2 g of the trans-anti-trans keto ester (X), m.p. 88-90°, undepressed by the sample prepared as above.

Clemmensen Reduction of the trans-anti-trans Keto Diester (X)

A mixture of 2.2 g of amalgamated zinc, 4 ml of concentrated hydrochloric acid, 4 ml of methanol, and 1.3 g of the trans-anti-trans keto diester (X) was boiled for three hours, and a further addition of 2 ml of concentrated hydrochloric acid was then made and the mixture was boiled further for 15 hours. Methanol was distilled off under reduced pressure, and the oil that separated was extracted with benzene. Solvent was distilled off, and vacuum distillation of the residue gave 1.1 g of a viscous oil, b.p. 152-153° (5 mm), which slowly solidified. Crystallization from a little petroleum ether gave 0.8 g of the dimethyl ester of trans-anti-trans-decahydro-1.2-naphthalenedicarboxylic acid (XI), m.p. 53-55°, undepressed by admixture of the sample obtained previously [3].

Reaction of the anti-cis Acetoxy Anhydride (III) with Methanol

A mixture of 5.2 g of the anti-cis acetoxy anhydride (III) and 25 ml of absolute methanol was boiled for one hour, methanol was distilled off under reduced pressure, and the crystalline residue was carefully washed on the filter with a mixture of diethyl ether and petroleum ether. The product (3.3 g) was the anti-cis acetoxy monoester (XVII), which melted at 180-181° after crystallization from acetone.

Found %: C 60.80; 60.90; H 6.92; 6.82 $C_{15}H_{20}O_6$. Calculated %: C 60.80; H 6.80

The washing were evaporated to half bulk, and on the next day 0.65 g of the isomeric anti-cis acetoxy monoester (XVI) had separated. It melted at 144-145° after crystallization from 50% aqueous acetone.

Found %: C 61.0; 68.84; H 6.74; 6.80 $C_{15}H_{20}O_6$. Calculated %: C 60.80; H 6.80

Transformations of the Isomeric anti-cis Acetoxy Monoesters (XVI) and (XVII)

a) The anti-cis acetoxy monoester (XVII) (2.2 g) was added to a solution of 0.26 g of sodium in 50 ml of absolute methanol and the mixture was boiled for four hours. It was then acidified with acetic acid, methanol was distilled off under reduced pressure, and the residue was dissolved in 10 ml of water. On the next day 1.1 g of crystals had separated; they melted at 164-168° after being dried in a vacuum. Two crystallizations from 50% acetone gave 0.7 g of the trans-anti-trans keto monoester (XVIII), m.p. 171-173°.

Found %: C 61.48; 61.25; H 7.15; 7.14 $C_{13}H_{18}O_5$. Calculated %: C 61.40; H 7.13

When treated with diazomethane, this keto monoester gave a quantitative yield of the previously obtained (above) trans-anti-trans keto diester (X), m.p. 89-90°.

b) By an analogous procedure, 0.2 g of the isomeric anti-cis monoester (XVI), after boiling with sodium methoxide and treatment of the residue with diazomethane, gave a liquid reaction product, from which the trans-anti-cis keto diester (VIII) was isolated in the form of its 2,4-dinitrophenylhydrazone, m.p. 214-215°, undepressed by admixture of the sample described above.

SUMMARY

1. The condensation of 1-(1-acetoxyvinyl)cyclohexene (I) with maleic anhydride was studied: it results in an 80% yield of the anti-cis anhydride (III), which is quantitatively hydrolyzed by water to anti-cis-4-acetoxy-1,2,3,5,6,7,8,8a-octahydro-1,2-naphthalenedicarboxylic acid (IV), which gives the anti-cis acetoxy diester (V) with diazomethane.

2. By hydrolysis of the acetoxy group in the acid (IV) and the diester (V) we prepared the trans-anti-cis keto acid (VI) and the trans-anti-trans keto diester (X), and Clemmensen reduction of these gave the previously described trans-anti-cis decahydro-1,2-naphthalenedicarboxylic acid (IX) and the trans-anti-trans decahydro-1,2-naphthalenedicarboxylic diester (XI), thus confirming the configurations of these last compounds.

3. The steric transformations of some monoesters of this series were studied, and it was shown that they readily undergo isomerization at the 2-alkoxycarbonyl group.

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ARYL VINYL ETHERS

COMMUNICATION 5. SOME PROPERTIES OF 2-NAPHTHYL VINYL ETHER

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This paper reports a further investigation on the properties and reaction of aryl vinyl ethers $CH_2=CH-OAr$. It was established previously [1] that aryl vinyl ethers differ from alkyl vinyl ethers in their behavior in several reactions. This is shown in the lower activity of aryl vinyl ethers in reactions that proceed by an ionic mechanism. The effect of an aryl radical is shown still more clearly in the behavior of the aryl 1-chloroethyl ethers obtained by the hydrochlorination of vinyl ethers [2]. These compounds are extremely reactive owing to the high mobility of the 1-chloro atom [3-5]. In spite of the fact that there is much in common in the behavior of alkyl and aryl 1-haloethyl ethers, there are some differences in the properties of these compounds. Decomposition, replacement of chlorine by bromine by the action of bromine or hydrogen bromide on the α-chloro ethers, reaction of the latter with alcohols – all these changes require different conditions or take a different course [2, 6]. All this indicates that the presence of the benzene nucleus retards ionic reactions of aryl 1-haloethyl ethers.

2-Naphthyl vinyl ether interested us as a little studied aryl vinyl ether. As the molecule of 2-naphthyl vinyl ether contains a radical that is a system of two condensed benzene nuclei, it would be expected that in this substance the properties of aryl vinyl ethers would be found in an intensified form.

The only reference in the literature to the preparation of 2-naphthyl vinyl ether is in a patent [7]. Braun and Kirschbaum [8] obtained it in 1920 by alkaline splitting of a quaternary ammonium base:

$$C_{10}H_7O-CH_2-CH_2-\underset{\displaystyle I}{\overset{\displaystyle (CH_3)_2}{\overset{|}{N}<}}{}_{C_6H_5} + KOH \rightarrow CH_2=CH-OC_{10}H_7 + (CH_3)_2NC_6H_5 + KI + H_2O. \quad (1)$$

Braun and Kirschbaum obtained the starting substance by a complex multistage synthesis in which the overall yield of the final product was extremely low.

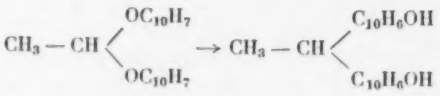
We prepared 2-naphthyl vinyl ether from 2-naphthol and acetylene by the Favorsky-Shostakovsky method [9] in 73% yield. The properties of 1-naphthyl vinyl ether were studied with respect to hydrolysis, hydrohalogenation, and alcohol-addition reactions.

The reaction of hydrogen chloride with 2-naphthyl vinyl ether was studied under the conditions that we established previously [2]. The product, 1-chloroethyl 2-naphthyl ether, is a white crystalline substance which fumes in the air and melts with decomposition at about 20°; it cannot be preserved in the pure state even at a low temperature in an atmosphere of dry nitrogen. The characterization of the 1-chloroethyl 2-naphthyl ether obtained – titration with 0.1 N NaOH and determination of chlorine and acetaldehyde in its hydrolyzate – was carried out on the freshly prepared material, and good results were always obtained.

When kept in the air, heated, or exposed in ethereal solution to the action of a stream of dry nitrogen or ammonia, the substance decomposed with elimination of hydrogen chloride and formation of an amorphous solid.

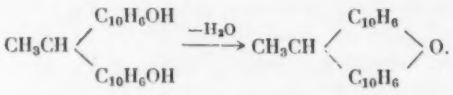
After being reprecipitated with methanol, this substance did not contain chlorine and melted at 196°. It was not affected by long boiling with 20-40% acids, and on distillation it resinified with elimination of a little 2-naphthol. The substance was probably a dimer of 2-naphthyl vinyl ether.

In its reactions with sodium ethoxide and with ammonia in presence of alcohol or 2-naphthol, 1-chloroethyl 2-naphthyl ether showed a peculiar property. Instead of the expected alkyl naphthyl or dinaphthyl acetal, in all cases the dialkyl acetal was obtained and a crystalline substance formed which corresponded in physical properties and analysis to 14-methyl-14H-dibenzo [a,j] xanthene. This compound was first isolated by Claisen in 1886 in the condensation of paraldehyde with 2-naphthol in glacial acetic acid in presence of concentrated hydrochloric acid [10]. In Claisen's opinion [12], the dinaphthyl acetal of acetaldehyde formed in the reaction is unstable and undergoes rearrangement to 1,1' -ethylidenedi(2-naphthol) :



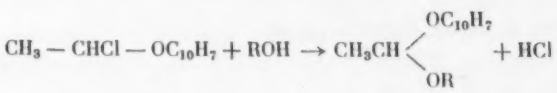
(2)

This compound readily loses water with ring closure:

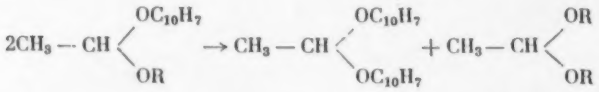


(3)

Under the conditions of our experiments on the reaction of 1-chloroethyl 2-naphthyl ether with alcohols, it is most probable that a mixed alkyl 2-naphthyl acetal was formed and then underwent disproportionation with formation of two symmetrical acetals : the di-2-naphthyl and dialkyl acetals:



(4)



(5)

The di-2-naphthyl acetal then underwent rearrangement with formation of 14-methyl-14H-dibenzo [a,j] xanthene (Equations 2 and 3) which was isolated in good yield together with the dialkyl acetal. Reaction of 2-naphthyl vinyl ether with alcohols in an acid medium again did not lead to the formation of mixed acetals: theoretical yields were obtained of 14-methyl-14H-dibenzo [a,j] xanthene and of the symmetrical acetal corresponding to the alcohol used. This fact confirms the scheme we have given for the reaction of 1-chloroethyl 2-naphthyl ether with alcohols.

Attempts to obtain mixed acetals from 2-naphthyl vinyl ether and alcohols by catalytic and thermal methods were not successful: the components were recovered unchanged, or 14-methyl-14H-dibenzo [a,j] xanthene was formed, or —when very severe conditions were used —resinification occurred.

All the 2-naphthyl acetals that we synthesized were obtained from 2-naphthol and the corresponding vinyl ether in presence of acid catalysts (see Table 1). It was observed on several occasions that prolonged keeping of alkyl 2-naphthyl acetals resulted in the formation of crystals of 14-methyl-14H-dibenzo [a, j] xanthene, which was identified by comparison with a pure preparation.

The difficulty of obtaining mixed alkyl naphthyl and aryl naphthyl acetals can be explained by the differing extents to which oxonium properties are exhibited by alkyl vinyl and aryl vinyl ethers. It is probable that acetals are formed via intermediate complexes :

$$CH_2 = CH - O - Alk \quad (6)$$
$$\vdots$$
$$HOAr$$

and

$$CH_2 = CH - OAr \quad (7)$$
$$\vdots$$
$$HOAr$$

the existence of which is less probable for aryl vinyl ethers (Equation 7).

TABLE 1
Characteristics of 2-Naphthyl Acetals Obtained

Name of acetal	Yield (%)	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	MR Found	MR Calculated	Elementary analysis Found (%) C	Found (%) H	Calculated (%) C	Calculated (%) H	Molecular weight Found	Molecular weight Calculated
Naphthyl phenyl	74.2	183(1)	1.6139	1.1282	80.52	78.43	81.66 81.61	6.09 6.13	81.79	6.16	263.3 255.7	264.33
Ethyl naphthyl	83.0	168(11)	1.5762	1.0369	69.02	69.05	78.14 77.96	7.14 7.20	77.78	7.47	207.6 212.1	216.23
Cyclohexyl naphthyl	62.3	165(1)	1.5670	1.0720	80.17	81.30	79.68 79.71	8.23 8.28	77.99	8.23	256.7 261.5	270.3

EXPERIMENTAL

1. Synthesis of 2-Naphthyl Vinyl Ether. A mixture of 50 g of 2-naphthol (m.p. 121°), 30 ml of water, and 16.5 g of potassium hydroxide powder was prepared in a 500-ml rotating autoclave. Acetylene was passed into the autoclave in portions, the initial pressures being 17-18 atm. Absorption of acetylene proceeded at 184-188°. When reaction was complete, steam distillation, drying, and vacuum distillation gave 42.5 g (73%) of 2-naphthyl vinyl ether; b.p. 114° (5 mm); b.p. 147° (22 mm); m.p. 34°; n_D^{20} 1.6172 (in a supercooled state); d_4^{20} 1.0612.

Found %: C 84.44; 84.31; H 6.02; 6.08 $C_{12}H_{10}O$. Calculated %: C 84.67; H 5.93

Found %: M 169.03 $C_{12}H_{10}O$. Calculated: M 170.21

2-Naphthyl vinyl ether is a white crystalline substance, m.p. 34°. It has a pleasant odor, and it can be preserved in the state of a supercooled liquid.

2. Hydrolysis of 2-Naphthyl Vinyl Ether. A weighed sample of 2-naphthyl vinyl ether was placed with 25 ml of 2% sulfuric acid in a tube, which was sealed and heated with shaking in a boiling water bath for two hours. The acetaldehyde content of the hydrolyzate was then determined by the bisulfite [1] or hydroxylamine method [13]. Ether content found : 98.76; 97.61%.

3. Synthesis of 1-Chloroethyl 2-Naphthyl Ether. An ethereal solution of 10 g of 2-naphthyl vinyl ether was introduced into a three-necked flask fitted with thermometer, stirrer, and reflux condenser. The solution was cooled to −7° and stirred vigorously while a stream of dry hydrogen chloride was passed until saturation was attained (five hours). The reaction mixture was transferred to a distillation flask and solvent was drawn off

in a stream of dry nitrogen. The residue in the flask (11.65 g) was a dry white powder which fumed in the air; m.p. 18-20° with decomposition.

Found %: M 206.0; 208.1 $C_{12}H_{11}OCl$. Calculated: M 206.72

Found % titratable H 100.21; 100.32 (0.1 N NaOH)

Found %: Cl 16.84; 16.94 (Volhard 's method) Calculated %: Cl 17.17

Found %: Cl 17.82; 17.85 (Mohr's method) Calculated %: Cl 17.17

Yield of 1-chloroethyl 2-naphthyl ether: 96.3%.

4. Reactions of 1-Chloroethyl 2-Naphthyl Ether. a) Decomposition. 1-Chloroethyl 2-naphthyl ether (10 g) was heated in a stream of nitrogen at low pressure at 100°. There was an immediate vigorous evolution of hydrogen chloride. When reprecipitated with methanol, the residue gave 7.3 g (89%) of a substance which melted at 196-197° after being dried in a vacuum desiccator.

Found %: C 84.40; 84.29; H 5.82; 5.93 $(C_{12}H_{10}O)_2$. Calculated %: C 84.71; H 5.88

Found : M 332.9; 329.7 $(C_{12}H_{10}O)_2$. Calculated: M 340.42

A dimer identical to the above was obtained in good yield also by keeping 1-chloroethyl 2-naphthyl ether in an atmosphere of nitrogen at + 4° for a short time and by passage of dry ammonia through an ethereal solution of 1-chloroethyl 2-naphthyl ether.

b) Reaction with ammonia in presence of 2-naphthol. A solution of 5 g of 1-chloroethyl 2-naphthyl ether in dry ether was mixed in the cold with 5 g of freshly distilled 2-naphthol. The mixture was placed in a flask fitted with reflux condenser and a stream of dry ammonia was passed through until the mixture was saturated. Absorption of ammonia was accompanied by evolution of heat and formation of a voluminous precipitate, which was allowed to stand overnight and then filtered off, washed free from ammonium chloride with water, and dried. Crystals isolated from the filtrate after removal of solvent were added to the bulk of the product, which then amounted to 6.12 g (86%) and had m.p. 173-174°.

Found : M 294.7; 292.5 $C_{22}H_{16}O$. Calculated: M 296.37

Found %: C 89.20; 89.09; H 5.52; 5.59 $C_{22}H_{16}O$. Calculated %: C 89.16; H 5.61

The product was 14-methyl-14H-dibenzo[a,j]xanthene, which the literature [11] describes as prismatic crystals, m.p. 173°.

c) Reaction with ammonia in presence of butyl alcohol. The reaction was carried out under the conditions of the preceding experiment. Ammonia was passed for one hour through a mixture of 8 g of 1-chloroethyl 2-naphthyl ether and 6 g of butyl alcohol, and the precipitate was filtered off. Vacuum fractionation of the filtrate gave 2.2 g (69.2%) of acetaldehyde dibutyl acetal, b.p. 183-183.5°, n_D^{20} 1.4076; and d_4^{20} 0.8241. The literature [14] gives b.p. 184-185°, n_D^{20} 1.4090; d_4^{20} 0.8267. The precipitate, after removal of ammonium chloride and recrystallization, gave 4.3 g (75.4%) of 14-methyl-14H-dibenzo[a,j] xanthene, m.p. 172°, undepressed by admixture of a pure sample of this substance.

d) Reaction with sodium ethoxide. 1-Chloroethyl 2-naphthyl ether (15 g) was added dropwise to alcoholic sodium ethoxide prepared from 1.7 g of sodium. The mixture was heated to 42°. The precipitate was filtered off, washed with ether and with water, and dried. Reprecipitation with methanol gave 3.2 g (25%) of a substance of m.p. 196°, identical with the dimer of 2-naphthyl vinyl ether characterized above. Solvent was distilled from the filtrate, and a crystalline precipitate formed; after recrystallization it had m.p. 173°, undepressed by admixture of pure 14-methyl-14H-dibenzo [a,j] xanthene. The yield was 5 g (47.5%). Fractionation of the filtrate gave 1.3 g (40.2%) of acetaldehyde diethyl acetal, b.p. 103-103.5° and n_D^{20} 1.3804. The literature [14] gives: b.p. 103-104°; n_D^{20} 1.3820; d_4^{20} 0.8254.

5. Reaction of 2-Naphthyl Vinyl Ether with Phenol. A solution of 10 g of 2-naphthyl vinyl ether and 5.8 g of phenol in benzene was prepared in a flask fitted with stirrer. Concentrated hydrochloric acid (4 drops) added, and the temperature rose to 50°; this temperature was maintained for five hours. Solvent was distilled off, and further distillation gave 3 g of unchanged phenol (m.p. 41°) and a crystalline substance, m.p. 171° after recrystallization from alcohol. It was found to be the above-described 14-methyl-14H-dibenzo [a,j] xanthene;

the yield was 7.19 g (82%).

6. Preparation of 2-Naphthyl Acetals of Acetaldehyde. Ethyl 2-naphthyl, cyclohexyl 2-naphthyl, and 2 naphthyl phenyl acetals of acetaldehyde were prepared in good yield in the same way as the butyl 2-naphthyl acetal [15] by reaction of 2-naphthol with ethyl vinyl, cyclohexyl vinyl, and phenyl vinyl ethers in presence of concentrated hydrochloric acid. For the characteristics of the acetals obtained see Table 1.

SUMMARY

1. 2-Naphthyl vinyl ether was prepared and investigated. The conditions were found for its complete hydrolysis, and this reaction can be recommended for the quantitative determination of the concentration of 2-naphthyl vinyl ether.

2. Some derivatives of 2-naphthyl vinyl ether were synthesized and characterized. These included 1-chloroethyl 2-naphthyl ether, and it was shown that this substance can be titrated quantitatively as HCl by various methods.

3. A study was made of the decomposition of 1-chloroethyl 2-naphthyl ether under various conditions. It was shown that elimination of HCl with dry ammonia is accompanied by the formation of a product corresponding in composition to the dimer of 2-naphthyl vinyl ether. In alcoholic media this reaction leads to the isolation of 14-methyl-14H-dibenzo [a, j] xanthene and acetaldehyde dialkyl acetal, which proves that mixed alkyl naphthyl acetals are formed in the first stage of reaction. Probable reaction schemes are proposed.

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ARYL VINYL ETHERS

COMMUNICATION 6. SOME PROPERTIES AND REACTIONS OF CYCLOHEXYL VINYL ETHER AND ITS DERIVATIVES

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The investigation of the reactions of cyclohexyl vinyl ether is of interest from the point of view of the comparison of the properties of alkyl, cyclohexyl, decahydronaphthyl, phenyl, and naphthyl vinyl ethers. The literature contains various information on the preparation of cyclohexyl vinyl ether [1, 2] and on some of its reactions, namely, its polymerization in presence of ferric chloride [3] and of 2,2'-azobis [2-methylpropionitrile] [4] and its addition reaction with hydrogen sulfide [5].

The present paper is devoted to a study of the properties of cyclohexyl vinyl ether as revealed in reactions of hydrolysis and of addition of hydrogen chloride, carbon tetrachloride, alcohols, and phenols. Particular attention was devoted to the properties of 1-chloroethyl cyclohexyl ether and of the products of reaction between cyclohexyl vinyl ether and carbon tetrachloride.

Treatment of cyclohexyl vinyl ether with 2% sulfuric acid at room temperature results in its complete hydrolysis. Addition of hydrogen chloride proceeds smoothly at a low temperature [6] and gives a good yield of 1-chloroethyl cyclohexyl ether. This ether can be preserved in the pure state only in sealed tubes in the cold; in presence of diluents it can be preserved at room temperature [7]. With excess of water 1-chloroethyl cyclohexyl ether breaks down into hydrogen chloride, acetaldehyde, and cyclohexanol.

In order to compare the action of ammonia on various α-chloro ethers, this reaction was carried out with 1-chloroethyl cyclohexyl, butyl 1-chloroethyl, and 1-chloroethyl phenyl ethers. When treated with dry ammonia, 1-chloroethyl cyclohexyl ether, like chloro derivatives of alkyl vinyl ethers, lost hydrogen chloride and formed the dicyclohexyl acetal of acetaldehyde. 1-Chloroethyl phenyl ether decomposed entirely and gave hydrogen chloride and phenol. The known exchange reaction between α- chloro ethers and Grignard reagents [8] was carried out in our case with butylmagnesium bromide and resulted in the formation of the corresponding 1-methylpentyl ethers. For comparison purposes this reaction was carried out with 1-chloroethyl cyclohexyl, butyl 1-chloroethyl, and 1-chloroethyl phenyl ethers.

It is known also that vinyl ethers react with carbon tetrachloride with formation of addition products [9] which, depending on the relative amounts of the reactants, may result from equimolecular (I) or polymeric (II) addition:

$$CCl_3 - CH_2CHCl - OR \qquad \text{and} \qquad CCl_3 - CH_2 - \underset{\underset{OR}{|}}{CH}\,[CH_2 - \underset{\underset{OR}{|}}{CH}]_n\,Cl.$$

(I) (II)

Cyclohexyl vinyl ether reacts with carbon tetrachloride in this way, giving products of types (I) and (II) (Table 1), depending on the conditions. Under the conditions of vacuum distillation cyclohexyl 1,3,3,3-tetrachloropropyl ether (I) readily decomposes, being different in this respect from alkyl and phenyl 1,3,3,3- tetrachloropropyl ethers; we were therefore unable to isolate it in the pure state. The formation of (I) was proved

by the isolation of a mixed cyclohexyl acetal (III) of 3,3,3-trichloropropionaldehyde in the reaction between the cryde tetrachloro ether and an alcohol:

$$CCl_3 - CH_2 - CHCl - OC_6H_{11} + ROH \rightarrow CCl_3 - CH_2 - CH\begin{matrix}OC_6H_{11}\\OR\end{matrix}$$

(III)

TABLE 1

Reaction between Cyclohexyl Vinyl Ether (CVE) and Carbon Tetrachloride in presence of Benzoyl Peroxide

No.	Molar ratio CVE/ CCl_4	Initial reaction temperature (°C)	Yield: cyclohexyl 1,3,3-trichloroallyl ether (%)	Yield: 3,3-dichloroacrolein dicyclohexyl acetal (%)	Yield: polymer (% on original mixture)
1	1 : 6	76	60	20.8	3.9
2	1 : 4	70	68	19.8	1.1
3	1 : 2	76	56	19.5	8.3
4	6 : 1	80	—	—	45.7

In the vacuum distillation of cyclohexyl 1,3,3,3-tetrachloropropyl ether, elimination of hydrogen chloride occurred, and cyclohexyl 1,3,3-trichloroallyl ether (IV) was formed and was isolated in good yield:

$$CCl_3 - CH_2 - CHCl - OR \rightarrow HCl + CCl_2 = CH - CHCl - OR.$$

(IV)

Cyclohexyl 1,3,3-trichloroallyl ether is stable, but its α-chlorine atom is very reactive and has many of the properties of the α-chlorine in alkyl 1-chloroethyl and 1-chloroethyl phenyl ethers. The tendency for (IV) to undergo hydrolysis is so great that it can be titrated quantitatively with alkali and the 3,3-dichloroacrolein formed can be characterized in the form of a derivative:

$$CCl_2 = CH - CHCl - OC_6H_{11} + H_2O \rightarrow CCl_2 = CH - CHO + C_6H_{11}OH + HCl$$

(V)

In reactions with alcohols and alkoxides, cyclohexyl 1,3,3-trichloroallyl ether forms mixed alkyl cyclohexyl acetals of 3,3-dichloroacrolein:

$$CCl_2 = CH - CHCl - OC_6H_{11} + ROH \rightarrow CCl_2 = CH - CH\begin{matrix}OR\\OC_6H_{11}\end{matrix} + HCl$$

(VI)

When heated, these compounds disproportionate with formation of two symmetrical acetals, and on hydrolysis they give 3,3-dichloroacrolein and the corresponding alcohols:

$$CCl_2 = CH - CH\begin{matrix}OC_6H_{11}\\OR\end{matrix} + H_2O \rightarrow ROH + C_6H_{11}OH + CCl_2 = CH - CHO.$$

(VII)

The products of polymeric addition of carbon tetrachloride and cyclohexyl vinyl ether, which are obtained under suitable conditions, are light-colored solid polymers containing chlorine and having molecular weight of 5000-7000. The activating role of carbon tetrachloride in this reaction was proved by control experiments carried out under the same conditions but in absence of carbon tetrachloride; in these experiments no polymer formation occurred.

In presence of traces of hydrochloric acid, cyclohexyl vinyl ether readily reacts with alcohols and phenols [10] with formation of mixed acetals (Table 2), which are pleasantly smelling liquids. These acetals are hydrolyzed by 2% sulfuric acid, and they disproportionate during storage and when distilled.

EXPERIMENTAL

The Cyclohexyl vinyl ether used had the following constants: b.p. 64° (35 mm); n_D^{20} 1.4541; d_4^{20} 0.8890.

Hydrolysis of Cyclohexyl Vinyl Ether

A weighed amount of cyclohexyl vinyl ether and 20 ml of 2% H_2SO_4 were introduced into a 100-ml measuring flask. The mixture was shaken for 30 minutes and then made up to the mark with water. Titration with 0.1 N I_2 gave 100.64% CH_3CHO.

TABLE 2

Products of Reaction of Cyclohexyl Vinyl Ether with Alcohols and Phenols

Acetal of acetaldehyde	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	MR		Elementary analysis				Yield (%)
				Found.	Calc.	Found (%)		Calculated (%)		
						C	H	C	H	
Dicyclohexyl	134—135(12)	1.4672	0.9535	65.9	65.7	74.33 74.34	11.52 11.59	74.29	11.61	85.0
Cyclohexyl naphthyl	165 (1)	1.5670	1.0726	82.2	80.2	79.71 79.63	8.23 8.28	79.99	8.23	60.0
Cyclohexyl phenyl	142—143(10)	1.4940	0.9972	64.3	64.3	75.99 75.95	9.72 9.81	76.32	9.15	56.0
Cyclohexyl ethyl	61—62(13)	1.4560	0.9405	49.46	49.80	70.72 70.75	11.86 11.88	69.91	11.70	60.0

Reaction of Cyclohexyl Vinyl Ether with Hydrogen Chloride

Cyclohexyl vinyl ether (40 g) was cooled to − 5° and saturated with hydrogen chloride [7]. The product was vacuum-distilled in a stream of dry nitrogen. The product, amounting to 37.9 g (73.6%), was 1-chloroethyl cyclohexyl ether, b.p. 82.5-83° (14 mm); n_D^{20} 1.4598; d_4^{20} 1.0108; found MR 43.02; calculated for C_8H_5OCl MR 43.45; found M 155.9; 155.3; calculated M 162.67.

1-Chloroethyl cyclohexyl ether is a pungently smelling liquid that fumes in the air.

1. Hydrolysis of 1-Chloroethyl Cyclohexyl Ether. A sealed tube containing a weighed amount (0.2-0.3 g) of 1-chloroethyl cyclohexyl ether was placed in a flask provided with a ground stopper and containing 25 ml of distilled water. The tube was broken, the contents of the flask were mixed carefully, and determinations of HCl and CH_3CHO were carried out. Titration with 0.1 N NaOH gave: titratable H 97.57; 98.00%.

Found %: Cl 21.00; 20.96 (Volhard method) $C_8H_{15}OCl$. Calculated %: Cl 21.12

The bisulfite method gave CH_3CHO 98.73; 99.34%.

2. Reaction of α-Chloro Ethers with Ammonia. a) 1-Chloroethyl cyclohexyl ether. 1-Chloroethyl cyclohexyl ether (17 g) was placed in a flask fitted with reflux condenser and tube for passage of gas; the flask was cooled with ice. A stream of dry ammonia was passed into the flask to saturation point. Ammonium chloride was filtered off, washed with ether, and dried (5.3 g, which is the theoretical amount). Distillation of the filtrate gave 11.2 g (88.8%) of a substance having b.p. 134-135° (12 mm); 140° (14 mm); n_D^{20} 1.4672; n_D^{23} 1.4648; d_4^{20} 0.9535; found MR 65.94; calculated for $C_{14}H_{26}O_2$ MR 65.74.

Found %: C 74.05; 74.34; H 11.53; 11.56 $C_{14}H_{26}O_2$. Calculated %: C 74.29; H 11.61

The product was acetaldehyde dicyclohexyl acetal. It was hydrolyzed by shaking with 2% sulfuric acid for 40 minutes at room temperature; found iodometrically CH_3CHO 96.70; 97.23%.

b) Butyl 1-chloroethyl ether. The elimination of HCl was effected as described above. An 83% yield was obtained of the dibutyl acetal b.p. 74° (14 mm); n_4^{20} 1.4083; d_4^{20} 0.8250 [11]; NH_4Cl was isolated in 81% yield.

c) 1-Chloroethyl phenyl ether. From 20 g of 1-chloroethyl phenyl ether we obtained 7.1 g of NH_4Cl and 11.5 g (92%) of phenol, b.p. 77-78° (16 mm), m.p. 41°.

3. Reaction of 1-Chloroethyl Cyclohexyl Ether with Sodium Ethoxide. 1-Chloroethyl cyclohexyl ether (7 g) was added dropwise to sodium ethoxide prepared from 1 g of sodium and excess of ethanol in a flask fitted with stirrer, thermometer, and condenser. The temperature in the flask rose to 41°. The filtrate was vacuum-distilled, and ethanol was followed by 6.5 g of a fraction of b.p. 69-71° (17 mm). After two distillations it had b.p. 71° (17 mm); 62° (13 mm); n_D^{20} 1.4567; n_D^{18} 1.4580; d_4^{20} 0.9411; found MR 49.46; calculated for $C_{10}H_{20}O_2$ MR 49.80; found M 170.13; 169.71; calculated M 172.27.

Found %: C 70.72; 70.75; H 11.86; 11.88 $C_{10}H_{20}O_2$. Calculated %: C 69.92; H 11.70

The product isolated was acetaldehyde cyclohexyl ethyl acetal and was obtained in 74.1% yield.

4. Reaction of α-Chloro Ethers with Butylmagnesium Bromide. a) 1-Chloroethyl cyclohexyl ether. In a flask fitted with condenser, stirrer, and thermometer, 15 g of 1-chloroethyl cyclohexyl ether was added dropwise to an equimolecular amount of butylmagnesium bromide prepared from 2.25 g of magnesium and 14.1 g of butyl bromide. Stirring was continued further for one hour, and the mixture was left overnight and then decomposed with 10% hydrochloric acid. The organic layer was separated, washed with water, and dried over calcium chloride. Solvent was removed, and vacuum distillation gave 11.2 g of a fraction of b.p. 98-105° (16 mm), which after purification had the following constants: b.p. 104-105° (16 mm); n_D^{20} 1.4408; d_4^{20} 0.8533; found MR 57.08; calculated for $C_{12}H_{24}O$ MR 57.06; found M 180.00; 176.1; calculated M 184.31.

Found %: C 77.98; 77.80; H 13.10; 13.05 $C_{12}H_{24}O$. Calculated %: C 78.18; H 13.10

The product isolated was cyclohexyl 1-methylpentyl ether and was obtained in 60% yield.

b) Butyl 1-chloroethyl ether. Reaction of 17 g of butyl 1-chloroethyl ether under the above-described conditions gave 14.6 g (74.6%) of butyl 1-methylpentyl ether, b.p. 65° (15 mm); n_D^{20} 1.4088; d_4^{20} 0.7860; found MR 50.73; calculated for $C_{10}H_{22}O$ MR 50.12.

c) 1-Chloroethyl phenyl ether. Reaction of 15 g of 1-chloroethyl phenyl ether under similar conditions gave 14.3 g (80.4%) of 1-methylpentyl phenyl ether, b.p. 86° (4 mm); n_D^{20} 1.4901; d_4^{20} 0.9228; found MR 55.86; calculated for $C_{12}H_{18}OF_3$ MR 55.92; found M 170.4; 171.5; calculated M 178.28.

Found %: C 81.22; 81.34; H 10.10; 10.00 $C_{12}H_{18}O$. Calculated %: C 80.90; H 10.10

Reaction of Cyclohexyl Vinyl Ether with Carbon Tetrachloride.

(Molar ratio 1 : 4)

A mixture of 61.4 g (0.4 mole) of carbon tetrachloride, 12.6 g (0.1 mole) of cyclohexyl vinyl ether, and 1.1 g of benzoyl peroxide was prepared in a flask fitted with thermometer and stirrer. The mixture was stirred and heated to 70°. Reaction resulted in a rise in temperature to 88°, and the reaction mixture was left at this temperature for two hours. It was then cooled, and excess of carbon tetrachloride was driven off in a stream of dry nitrogen. Vacuum distillation of the residue gave 16.69 g of Fraction I, b.p. 106° (4 mm), and 3.07 g of

Fraction II, b.p. 152-153° (4 mm); the solid residue amounted to 3.93 g. Fraction I had n_D^{20} 1.5040; d_4^{20} 1.2412; found MR 58.08; calculated for $C_9H_{13}OCl_3$ MR 57.34; found M 239.2; 233.6; calculated M 243.57.

Found %: C 44.52; 44.56; H 5.36; 5.32 $C_9H_{13}OCl_3$. Calculated %: C 44.36; H 5.36

This substance was cyclohexyl 1,3,3-trichloroallyl ether and was obtained in 68% yield.

Fraction II had n_D^{20} 1.4987; d_4^{20} 1.1292; found MR 79.98; calculated for $C_{15}H_{24}O_2Cl_2$ MR 79.62.

Found %: C 59.06; 58.93; H 7.84; 7.90; Cl 22.66; 22.44 $C_{15}H_{24}O_2Cl_2$. Calculated %: C 58.60; H 7.81 Cl 23.13

This substance was 3,3-dichloroacrolein dicyclohexyl acetal and was obtained in 19.8% yield. The polymer (1.5 g) isolated from the residue contained chlorine.

a) Titration of Cyclohexyl 1,3,3-Trichloroallyl Ether with 0.1 N NaOH. A weighed amount of the ether was sealed in a tube with excess of distilled water, and the tube was heated at 90° for one hour. The contents of the tube were then transferred to a 200-ml flask, diluted with water, and titrated with 0.1 N NaOH. For titratable hydrogen we found 98.6; 96.62%.

b) Reaction of Cyclohexyl 1,3,3-Trichloroallyl Ether with Sodium Ethoxide. Cyclohexyl 1,3,3-trichloroallyl ether (16 g) was added dropwise with stirring to sodium ethoxide prepared by dissolving 1.51 g of sodium in excess of ethanol. The sodium chloride separated amounted to 3.90 g (100%). Vacuum distillation of the filtrate gave Fraction I, 1.5 g, b.p. 41-47° (2 mm); Fraction II, 7.6 g, b.p. 100-112.5° (2 mm); Fraction III, 3.1 g, b.p. 124-153° (2 mm); and residue, 4.5 g.

From Fraction I we isolated a substance having b.p. 46-47° (2 mm); n_D^{20} 1.4509; d_4^{20} 1.1482; found MR 47.65; calculated for $C_7H_{12}O_2Cl_2$ MR 47.08, which was found to be 3,3-dichloroacrolein diethyl acetal.

From Fraction II we isolated 6.6 g of a substance having b.p. 111.5-112.5° (2 mm); n_D^{20} 1.4647; d_4^{20} 1.1212; found MR 63.62, calculated for $C_{11}H_{18}OCl_2$ MR 63.35; found M 247.1; 248.3; calculated M 253.19.

Found %: C 52.68; 52.62; H 7.20; 7.26; Cl 27.08; 27.38 $C_{11}H_{18}OCl_2$. Calculated %: C 52.18; H 7.16 Cl 28.00

This substance was 3,3-dichloroacrolein cyclohexyl ethyl acetal, obtained in 39.6% yield. Hydrolysis of the acetal gave 3,3-dichloroacrolein, which was isolated as the semicarbazone, m.p. 164-165°, undepressed by admixture of a pure sample.

After being purified Fraction III had b.p. 139-140° (2 mm); n_D^{20} 1.4923; d_4^{20} 1.1262; found MR 79.12. It was 3,3-dichloroacrolein dicyclohexyl acetal and was obtained in 25% yield (2.7 g). It was characterized above.

c) Reaction of Cyclohexyl 1,3,3,3-Tetrachloropropyl Ether with Sodium Ethoxide. To 16 g of crude cyclohexyl 1,3,3,3-tetrachloropropyl ether an equimolecular amount of sodium ethoxide was added with stirring (as a solution in ethanol). The temperature of the reaction mixture rose to 32-35°. The mixture was set aside overnight. The precipitated sodium chloride (2.7 g, i.e., 81%) was filtered off, and the filtrate was vacuum-distilled. The main fractions were:

Fraction I, 5.3 g (57.3%), b.p. 64.5° (3 mm); n_D^{20} 1.4519; d_4^{20} 1.1972; found MR 52.94; calculated for $C_7H_{13}O_2Cl$ MR 52.41. This was 3,3,3-trichloropropionaldehyde diethyl acetal, which we have described previously [9]; the literature gives b.p. 80-81° (9 mm), n_D^{20} 1.4450; d_4^{20} 1.1836.

Fraction II, 6.8 g (37.4%), b.p. 122-122.5° (4 mm); n_D^{20} 1.4770; d_4^{20} 1.1882; found MR 68.72; calculated for $C_{11}H_{19}O_2Cl_3$ MR 68.68; found M 281.3; 280.2; calculated M 289.65.

Found %: C 46.42; 46.34; H 6.66; 6.62; Cl 35.90; 35.61 $C_{11}H_{19}O_2Cl$. Calculated %: C 45.95; H 6.61; Cl 36.72

This fraction consisted of 3,3,3-trichloropropionaldehyde cyclohexyl ethyl acetal.

Small amounts were isolated also of the diethyl (b.p. 53-56° (4 mm); n_D^{20} 1.4500) and dicyclohexyl (b.p. 162-166° (7 mm); n_D^{20} 1.4950) acetals of 3,3-dichloroacrolein, which were characterized above.

Reaction of Cyclohexyl Vinyl Ether with Carbon Tetrachloride

(Molar ratio 6 : 1)

A mixture of 22.68 g of cyclohexyl vinyl ether, 4.62 g of carbon tetrachloride, and 0.5 g of benzoyl peroxide was prepared in the reaction flask. The mixture was heated to 68°, and reaction then resulted in a rise in temperature to 86°; this temperature was maintained for two hours. Excess of carbon tetrachloride was distilled off, and the polymer was reprecipitated twice with methanol and vacuum-dried (9.45 g, i.c., 42%). The polymer was a light-yellow solid, soluble in ether, acetone, and benzene, but insoluble in methanol and ethanol. It contained about 1% of chlorine.

Found %: C 75.72; 75.79; H 11.08; 11.03 $C_8H_{14}O$. Calculated %: C 76.13; H 11.18

Found M 7226; 8065

Reaction of Cyclohexyl Vinyl Ether with Alcohols and Phenols

Equimolecular amount of cyclohexyl vinyl ether and the alcohol of phenol reacted in presence of traces of concentrated hydrochloric acid [1] with slight evolution of heat and gave a good yield of the mixed acetal. The characteristics of the acetals obtained are given in Table 2.

SUMMARY

1. The conditions were found for the hydrolysis of cyclohexyl vinyl ether, and for its reactions with hydrogen chloride, carbon tetrachloride, alcohols, and phenols. The products were characterized, and their structures were proved by hydrolysis and exchange reactions.

2. A study was made of some properties and reactions of 1-chloroethyl cyclohexyl ether, cyclohexyl 1,3,3,3-tetrachloropropyl ether, and cyclohexyl 1,3,3-trichloroallyl ether. In many reactions these substances behave analogously owing to the presence of α-chlorine in their molecules.

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TRANSFORMATIONS OF TOLUENE AND ETHYLBENZENE IN PRESENCE OF A NICKEL– ALUMINA CATALYST AND HYDROGEN UNDER PRESSURE IN A FLOW SYSTEM

N. I. Shuikin, N. G. Berdnikova, and L. K. Kashkovskaya

In a study of the behavior of some aromatic hydrocarbons in presence of platinum- and nickel-alumina catalysts at high temperature and under a high pressure of hydrogen we showed [1] that under these conditions a variety of transformations can occur.

As a development of this work we considered it to be of interest to study the behavior of toluene and ethylbenzene in presence of a nickel-alumina catalyst and hydrogen under pressure at high temperatures.

EXPERIMENTAL

In order to obtain toluene and ethylbenzene in a pure state they were distilled through a 42-plate column at 759 mm; they then had the following properties: toluene - b.p. 110.5°, n_D^{20} 1.4968 and d_4^{20} 0.8666; ethylbenzene - b.p. 136.2°, n_D^{20} 1.4960 and d_4^{20} 0.8672.

We have described the experimental procedure and the method of investigating the catalysis products previously [2, 3].

Catalytic Treatment of Toluene

Investigation of the transformations of toluene was carried out in presence of samples of finely dispersed nickel (1, 10, 20, and 30% Ni) deposited on activated alumina at 460° at a space velocity of 0.5 hour^{-1}, both under high pressures (25 and 50 atm) and also under atmospheric pressure of hydrogen. In all experiments the molar ratio of hydrogen to toluene was the same (about 5 : 1). In each experiment we took 200 ml of toluene, and for precise fractionation - 100 ml of catalyzate. Results obtained in the catalytic treatment of toluene are given in Table 1.

It follows from Table 1 that in the treatment of toluene in presence of 10, 20, and 30% nickel-alumina catalyst hydrogenolysis of the methyl group occurs with formation of benzene. This main reaction is accompanied by formation of xylenes, which were isolated by precise rectification of the catalyzates into fractions boiling in the range 136.5-146.5°. Ullmann oxidation [4] of the xylene fractions gave crystalline acids, and separation of these by the method described by Moldavsky and coworkers [5] gave benzoic acid (an insignificant amount, m.p. 121°), phthalic acid (m.p. 190°), isophthalic acid (m.p. of methyl ester 65°), and terephthalic acid (m.p. of methyl ester 140°), which shows that all three xylenes were present in the xylene fractions. The compositions of the xylene fractions isolated from the catalyzates of Experiments 1,2, and 3 are given in Table 2.

At the same time more profound transformations of toluene occur with formation of a small amount of cycloalkanes (methylcyclopentane and cyclohexane), which were detected by Raman spectra in the combined head fraction, b.p. 63-76.5°, d_4^{20} 0.7105; n_D^{20} 1.4001. When the content of finely dispersed nickel in the catalyst was reduced from 30 to 1%, the extent to which the transformation of toluene proceeded was greatly reduced (Table 1, Experiments 1 and 8).

It was of interest to compare the results of the catalytic treatment of toluene in presence of hydrogen under pressure with those obtained at ordinary pressure. It was shown by special experiments that at ordinary

TABLE 1
Properties of Toluene Catalyzates

Experiment	Ni content of catalyst (%)	Hydrogen pressure (atm)	Yield of catalyzate (% by weight)	n_D^{20}	d_4^{20}	Content (% by weight) in catalyzate			Composition of gas (STP) (%)	
						Unchanged toluene	Benzene	Xylenes	H_2	C_nH_{2n+2}
1	30	25	89.8	1.4966	0.8622	59	35.4	2.6	68	32
2	30	50	80.7	1.4946	0.8557	58.3	36.2	2.5	—	—
3	20	25	89.7	1.4965	0.8684	41.5	33.4	2.1	68	32
4	20	50	85.5	1.4950	0.8661	43.5	31.5	2.0	—	—
5	10	25	88.6	1.4959	0.8630	68.8	26.4	1.8	67	33
6	10	50	84.5	1.4956	0.8641	65.9	29.5	1.6	63	37
7	10	1	96.1	1.4965	0.8632	90.7	5.8	0.5	95	5
8	1	25	99.6	1.4970	0.8638	95.6	0.8	0.6	100	—
9	1	50	99.0	1.4965	0.8642	95.7	0.8	0.5	100	—

pressure the hydrogenolysis of toluene observed at 460° in presence of 10% nickel-alumina catalyst was much less: at a space velocity of 0.5 hour^{-1} 5.8% of the toluene was converted into benzene (Table 1, Experiment 7), whereas under the same conditions at a hydrogen pressure of 25 atm 26.4% of benzene was formed. When these results are compared, the part played by pressure in favoring rupture of the side link with formation of benzene is clearly seen. Hence, under our conditions part of the toluene undergoes transformations in accordance with the following scheme :

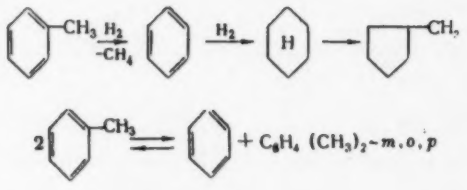
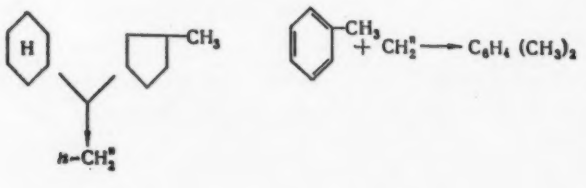


TABLE 2
Composition of Xylene Fractions on the Basis of Ullmann Oxidation

Experiment	Boiling limits of fraction (°C)	n_D^{20}	d_4^{20}	Amount taken for oxidation (g)	Content of xylenes (%)		
					m-xylene	p-xylene	o-xylene
1	137.0—146	1.4965	0.8647	2.6	47.0	30.0	15.0
2	136.5—145	1.4970	0.8652	2.5	53.0	29.6	11.2
3	137.0—146,5	1.4965	0.8650	2.1	54.5	28.0	9.8

We do not exclude the possibility of the formation of xylenes not only as a result of the transfer of methyl groups from one benzene nucleus to another, but also by methylation of toluene molecules with methylene radicals formed at the surface of the catalyst by the methylene breakdown of cycloalkanes:



Catalytic Treatment of Ethylbenzene

Experiments with ethylbenzene were carried out under the same conditions as those with toluene. The properties of the ethylbenzene catalyzates are given in Table 3.

TABLE 3

Properties of Ethylbenzene Catalyzates

Experiment	Ni content of catalyst (%)	Hydrogen pressure (atm)	Yield of catalyzate (% by weight)	n_D^{20}	d_4^{20}	Content (% by weight) in catalyzate			Composition of gas (STP) (%)	
						Unchanged ethylbenzene	Benzene	Toluene	H_2	C_nH_{2n+2}
1	30	20	71.5	1.4980	0.8685	21.3	48.5	26.7	81.7	18.3
2	30	30	78.5	1.4980	0.8680	33.5	41.2	22.3	—	—
3	30	50	80.7	1.4960	0.8651	38.2	39.8	18.5	—	—
4	20	25	73.8	1.4980	0.8682	27.0	48.0	22.0	—	—
5	10	25	74.1	1.4980	0.8685	43.5	33.4	19.8	82.17	16.43
6	10	50	73.8	1.4960	0.8643	49.4	31.5	15.6	83.3	16.6
7	10	1	97.9	1.4985	0.8698	83.7	8.3	5.0	95.5	4.5
8	1	25	98.9	1.4970	0.8658	96.2	0.8	—	100.0	—
9	1	50	98.3	1.4975	0.8666	96.1	0.9	—	100.0	—
10 (pure Al_2O_3)	0	50	98.3	1.4980	0.8669	95.6	1.4	—	98.7	1.2

Table 3 shows that reduction in the nickel content of the catalyst from 30 to 1% leads to almost complete inability to bring about the dealkylation reaction (as in the case of toluene). Increase in the pressure to 25 atm (Table 3, Experiments 5 and 7) results in a considerable increase in the amounts of complete and partial dealkylation of ethylbenzene. Further increase in pressure to 50 atm has no further substantial effect on the character and extent of the transformations of ethylbenzene. It was shown by special experiments that ethylbenzene undergoes only slight changes at 460° and 50 atm in presence of only activated alumina.

In the main, ethylbenzene catalyzates obtained in presence of hydrogen at high pressure over catalysts containing 20 and 30% of nickel consisted of benzene and toluene. As in the catalytic treatment of toluene, some more profound transformations occurred with formation of appreciable amounts of xylenes (0.5-0.1% in Experiments 1-6) and of low-boiling fractions 63-78° and 81-105°. The yield of head fraction boiling at 63-78° from catalyzates of experiments carried out at 25 atm was 0.2-0.3% on the amount of catalyzate, and at 50 atm it attained 0.5-0.6%.

For the purpose of detailed investigation, head fractions boiling in the range 63-78° (753 mm) from catalyzates obtained in Experiments 1, 2, and 3 were combined (4.5 g). This combined fraction had n_D^{20} 1.4650; d_4^{20} 0.8215; it contained 40% of benzene. After removal of benzene by adsorption on silica gel, the remaining, dearomatized part of this fraction had n_D^{20} 1.4115; d_4^{20} 0.7507, and aniline point 36.5, which leads us to suppose that methylcyclopentane, cyclohexane, and probably C_6 alkanes were present.

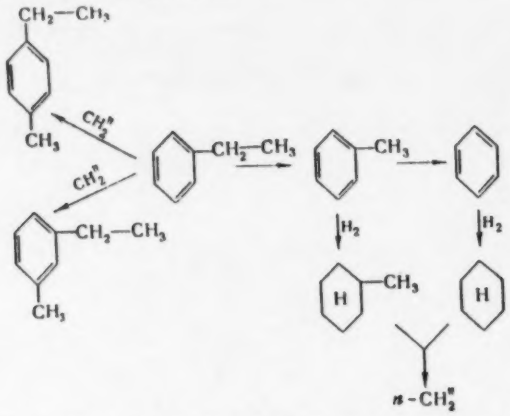
The intermediate fractions of the catalyzates of Experiments 1, 2 and 3 (Table 3), boiling range 81-105°, were also combined. The properties of this combined fraction (n_D^{20} 1.4850 and d_4^{20} 0.8357) gave use reason to suppose that it contained benzene, toluene, and some methylcyclohexane. In order to prove this supposition, the combined fraction of b.p. 81-105° was subjected to dehydrogenational catalysis by Zelinsky's method in presence of platinized charcoal containing 4.5% Pt. This gave a catalyzate of n_D^{20} 1.4980 which contained toluene. It follows that one component of this fraction was methylcyclohexane.

The residues obtained in the fractionation of the catalyzates of Experiments 1, 2, and 3 were combined. Fractionation of the mixture at 753 mm gave the following fractions:

Fraction I: b.p. 147-165°; 2.8 g; n_D^{20} 1.4960; d_4^{20} 0.8639
Fraction II: b.p. 165-173°; 2.5 g; n_D^{20} 1.5020; d_4^{20} 0.8693
Fraction III: b.p. 173-185°; 1.8 g; n_D^{20} 1.4990; d_4^{20} 0.8647

Oxidation of these fractions with alkaline potassium permanganate solution gave isophthalic and terephthalic acids, and by separation of these by the method described by Moldavsky and coworkers [5] we succeeded in showing the presence of 1-ethyl-3-methylbenzene and 1-ethyl-4-methylbenzene in Fraction I and 1,3- and 1,4-dialkylbenzenes in Fraction III.

The results of the investigation of the catalyzates give us grounds for the following scheme of transformations of ethylbenzene in presence of nickel-alumina catalysts:



Under our conditions the main transformation of ethylbenzene is partial and complete hydrogenolysis (dealkylation) of the side group with formation of toluene and benzene.

SUMMARY

1. A study was made of the transformations of toluene and ethylbenzene at 460° in presence of hydrogen at 25 or 50 atm over nickel-alumina catalysts of different nickel contents.

2. It was found that lowering of the nickel content of the catalyst from 30 to 1% results in almost complete elimination of transalkylation reactions and of the hydrogenolysis of the side chains of toluene and ethylbenzene.

3. The transformations of toluene and ethylbenzene in presence of nickel-alumina catalysts containing 30, 20, and 10% of reduced nickel are accompanied by the formation of products of complete and partial dealkylation due to hydrogenolysis of side chains and are accompanied also by the synthesis of xylenes and ethylmethylbenzenes (from ethylbenzene), hydrogenation of the benzene nucleus to cyclohexane, and isomerization of the latter to methylcyclopentane.

4. It was shown that the extent to which hydrocarbons undergo transformation under given conditions (25 atm and 460°) increases with increase in their molecular weights: it is 38% for toluene and 76% for ethylbenzene.

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STRUCTURE OF THE CELLULOSE MOLECULE AND ITS DEGRADATION

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The properties of the macromolecular substance, cellulose, depend on the chemical structure of its molecule (structure of the monomer unit), the type of linkage between the units, the number of units, and also the way in which the chain molecules are packed together in the actual cellulose preparation. In the present paper we shall examine the available experimental data from the point of view of the principles underlying the generally accepted views on the molecular structure of cellulose, possible departures from this structure, the number of glucose units in the cellulose chain, and the degradation of the molecule under various conditions. Chemical, polarimetric, kinetic, and statistical investigations have shown that glucose units are linked together in the cellulose molecular chain through 1,4-β-glucosidic linkages [1].

The assumptions made in the calculations and the reproducibility of the experimental results are such that this conclusion may be in error by as much as 1%. Improvement in the accuracy of the mathematical treatment of the experimental data has enabled some investigators to conclude that the error is not more than 0.1% [2]. This means that the nature of one glucosidic link out of a thousand cannot be determined with certainty. It should be noted that even slight chemical modifications of the molecule can alter the properties of cellulose appreciably [3-12].

By 1941 it was generally held that in various preparations cellulose usually has a maximum degree of polymerization P of about 3000 [13-17]. Intensive investigations on the determination of the degree of polymerization, or fractionation, on oxidative and thermal degradation, and on the chemical composition of various celluloses have shown that the mean degree of polymerization of cellulose attains 5000-15000 (Table 1). Those bonds which have not been accounted for, comprising at least 0.1% of the total, are weaker than the remainder and therefore extremely reactive bonds that have a substantial influence on the chemical reactions of cellulose and on its physical properties. The high chemical and thermal sensitivity [11] of the weak bonds made their determination difficult and often gives rise to doubt about their existence.

The structural formula of cellulose proposed in 1929 by Haworth [25] in the form of a planar projection gives the best approximation to the basic experimental data. However, the development of science and industry in the last fifteen years has prompted numerous investigations with the object of obtaining a more accurate picture of the molecular structure of cellulose. Confirmation of the presence of weak places in the chain molecule of cellulose is to be found in the following facts and calculations based on them.

1. The considerable discrepancy between experimental and calculated results for the dependence of the distribution of heterogeneity u with respect to molecular weight on degree of polymerization for heterogeneous and homogeneous hydrolysis [5] (Fig. 1).

2. The presence of distinct maxima on curves relating the mass distribution of cellulose to degree of polymerization, as illustrated by Table 2.

3. The great difference in rates of acid hydrolysis of cellulose (by a factor of 10,000) in the initial and subsequent periods [26], illustrated by Fig. 2.

4. The discrepancy between experimental and calculated curves for the molecular distribution of mass, both for homogeneously (in H_3PO_4) and for heterogeneously (in $KHSO_4$ solution) hydrolyzed celluloses, illustrated by Figures 3 and 4 [5]. The similarity in the behaviors of celluloses hydrolyzed in homogeneous and heterogeneous conditions indicates that the weak bonds belong to the chain molecule.

TABLE 1

Degrees of Polymerization of Various Celluloses

No	System	Kind of cellulose	Method	Degree of polymerization	Year	Investigators
1	Cellulose in cuprammonium solution	Cotton	By viscosity, O_2 removed chemically	4000—4500	1940	Golova and Nikolaeva [18]
2	Ditto	Cotton	By viscosity, chemical and vacuum removal of O_2	10 000—15 000	1945	Golova and Ivanov [19]
3	Cellulose in cupriethylenediamine	Cotton	Osmometeric and viscosimetric	6200	1953	Mark [20]
4	Cellulose in cuprammonium solution Cellulose in cupriethylenediamine	Cotton	By ultracentrifuge	5200 5200	1953	Neumann, Loeb and Conrad [21]
5	Cellulose nitrate in acetone	Cotton	By light-scattering and viscosity	13 000 (highest fraction)	1953	Doty, Schneider, and Holtzer [22]
6	Cellulose nitrate in acetone	Conservatory cotton (no exposure to sunlight)	By ultracentrifuge	8300	1954	Meyerhoff [23]
7	Cellulose in cupriethylenediamine	Cotton, ramie, linen	Ditto	4500—5000	1955	Marx [24]
8	Cellulose nitrate in acetone	Birch cellulose	Viscosimetric	5500	1956	Timell [4]

5. Statistical treatment of electron-microscope data on the lengths of the fibril fragments obtained on hydrolysis showed the presence of a maximum at 2300 A corresponding to a chain of 450 glucose units [27-29].

6. Depolymerization of cellulose nitrate gels by ultrasonic vibrations resulted in the establishment of maxima on the distribution curves corresponding to a degree of polymerization of 1000. This maximum retains its position and increases in height as treatment continues [30].

The origin of weak links is associated, in the first place, with the biological structure [29] and, in the second place, with the process of isolating cellulose from accompanying substances [26, 31]. Schultz and

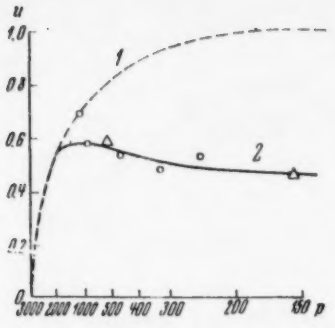


Fig. 1. Distribution of heterogeneity: 1) statistical (links homogeneous); Δ - cellulose hydrolyzed in a homogeneous medium (in H_3PO_4 at 29°); o - cellulose hydrolyzed in a heterogeneous medium (in $KHSO_4$ solution); 2) curve calculated taking weak links into account.

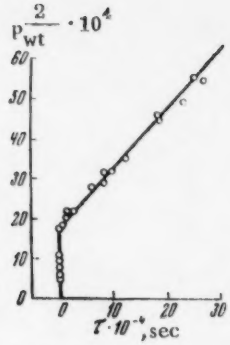


Fig. 2. Hydrolysis of Egyptian Cotton regenerated from cuprammonium solution in 0.1 N H_2SO_4 at 50°.

Husemann consider that weak links are formed in the course of the formation of cellulose in the plant as a result of the inclusion of pentose residues - formed by decarboxylation of acids - in the cellulose chain [5]. Actually, small amounts of D-xylose and L-arabinose have been found in various celluloses; thus, 0.33 and

TABLE 2

Mass Distribution of Cellulose from Fractionation Data

No.	Original cellulose	Number of maxima	Degree of polymerization	Year	Investigators
1	Native cotton cellulose hydrolyzed in H_3PO_4	2	500–1000	1942	Schulz and Husemann [5]
2	Cotton linters	1	1500	1951	Timell and Purves [6]
3	Mercerized linters	1	1100		
4	Methylated linters	1	800		
5	Beech cellulose	1	1500	1951	Asoaka, Sutuki, and Kudo [7]
6	Ditto	1	900		
7	Eucalyptus cellulose	3	500, 1000, 1500	1949	Emery and Cohen [9]
				1951	Schulz and Kounnerling [10]
8	Beech cellulose	2	500, 1000		
9	Cotton cellulose	2	500, 1000	1953	Bandel [11]
10	Sulfite pine cellulose	1	1000	1953	Lang [12]
11	Alkali-cellulose from pine	1	500		
12	Birch cellulose	1	3000		
13	Holocellulose from birch	1	3500	1956	Timell [4]

0.008%, respectively, of these carbohydrates have been found in hard-wood cellulose, but no pentoses have been found in cotton cellulose [31, 34]. We therefore cannot exclude the possibility of the presence of weak links in the molecular chains of wood celluloses arising from the inclusion of some pentose structural units.

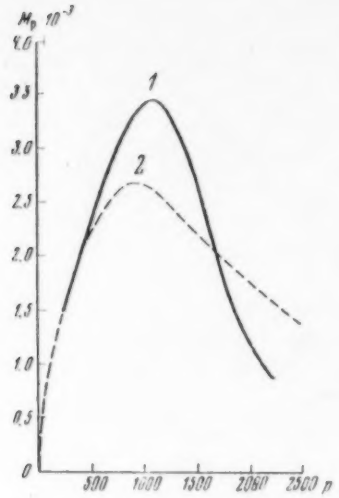


Fig. 3. Mass distribution for homogeneously hydrolyzed (in H_3PO_4) cellulose: 1) experimental data; 2) calculated values on assumption of statistical hydrolytic breakdown of glycosidic links.

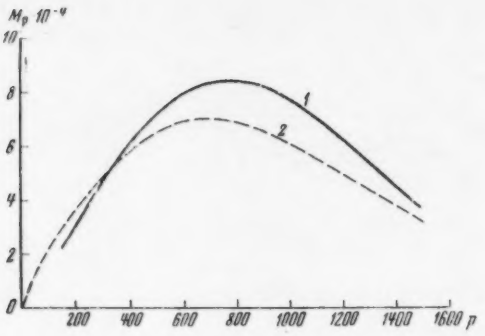
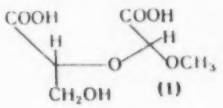


Fig. 4. Mass Distribution for heterogeneously hydrolyzed (in $KHSO_4$) cellulose: 1) experimental data; 2) calculated values on assumption of statistical hydrolytic breakdown of glycosidic links.

A study of the oxidative transformations of cellulose led us to the conclusion that a small proportion of the 1,4-β-glucosidic links may be weakened by the formation of carbonyl and carboxy groups in the glucose unit [31]. The presence of 7-14 carboxy groups per 10,000 glucose residues in the most carefully purified celluloses has been established by various authors [26, 35, 36]. We have shown that under all conditions of the oxidation of cellulose carboxy groups are formed in the 2-, 3-, and 6-positions[37-40]. We prepared α-D-(hydroxymethyl)-α'-D-methoxydiglycolic acid (I)



(I)

and investigation showed [31] that its hydrolysis occurs more readily than that of the usual glucosidic link. Among weak places with respect to acid hydrolysis we therefore include glucose residues of the chain molecule which have carboxy groups in the 2- and 3-positions.

Comparison of the values for the molecular weight of cellulose obtained by the end-group method and by viscosimetry in cuprammonium solution leads to the conclusion that the cellulose molecule contains extra aldehyde groups (2-3 per 1000 glucose units) within the chain and, as we have shown, this results in partial breakdown of the cellulose molecule in an alkaline medium [37-40]. This view of the chemistry of degradation was later confirmed by other investigators [41].

Hence, the molecules of cotton cellulose contain weak links associated with carbonyl and carboxy (in positions 2 and 3) groups formed during the separation of accompanying substances which inevitably occurs in an oxidizing medium. As already indicated, the molecules of wood celluloses contain also some structural units that are not based on glucose. The structure of the molecule of native cellulose, in the form in which it occurs in plant tissues, has not yet been established.

Hence, the study of the oxidative changes of cellulose and the properties of the products acquire considerable importance. We have studied the chemistry of the primary transformations of the cellulose molecule in its reactions with molecular oxygen, H_2O_2, N_2O_4, and hypochlorite [18, 19, 37-40, 42-52]. We have shown recently that data in the literature [53] on the selective oxidation of cellulose by N_2O_4 is in need of substantial

correction. The action of N_2O_4 on cellulose results not only in the formation of 6-carboxy groups, but also in the formation of nitric esters and keto groups [49]. The nitrogen content of such oxycelluloses varies about a mean of approximately 1%, which means that about 21 hydroxy groups are substituted for every 100 glucose units. These experimental results enable us to present a supplementary scheme for this case of the transformations and degradation of cellulose:

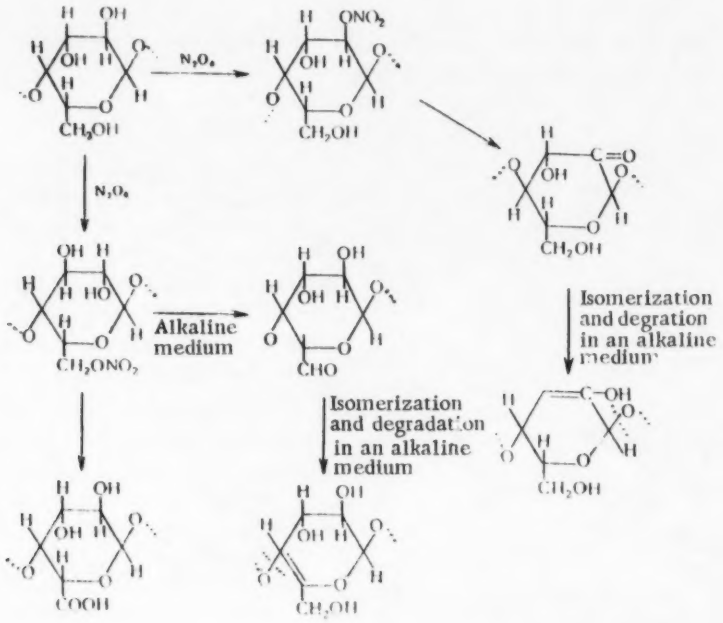


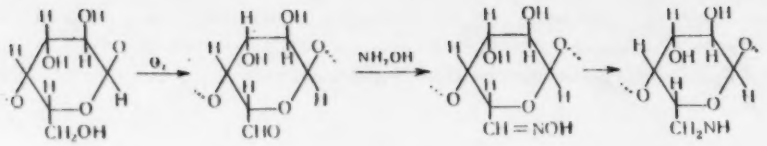
TABLE 3

Decarboxylation of Cellulose Preparations Oxidized with $NaIO_4$ and $NaClO_2$ (starting material: cotton cellulose)

Name of sample	COOH content (%) by Ca acetate method	Amount of CO_2 (%)
Cotton cellulose	0.06	0.14
Dicarboxycellulose		
No. 1	1.70	0.44
No. 3	8.20	0.70
No. 5	12.70	1.10
No. 6	14.70	1.20

We have shown that, in the preparation of dicarboxycelluloses by the oxidation of cellulose with $NaIO_4$ and further oxidation of the product with sodium chlorite, the main reaction [54] leading to the formation and opening of a pyran ring is accompanied by oxidation at C-6. This is confirmed by our results on the determination of uronic acids in these oxycelluloses by decarboxylation (Table 3) and by infrared spectrum data obtained in joint investigations by the Academy of Sciences of the USSR and the Belorussian University, which indicate that part of the CH_2 groups disappears in this reaction. A general feature of all oxidative transformations of cellulose is the introduction of various numbers of carboxy groups into the chain molecule.

The intermediate products of cellulose degradation - carboxy derivatives of cellulose - may find application in analytical, organic, and biological chemistry [50-52], particularly as ion-exchange agents. For example, in joint work with the Institute of Endocrinology, we succeeded in separating the proteins of adrenocorticotropic preparations on oxycellulose, thus isolating a fraction 8-10 times as active as the original preparation. There are possibilities of preparing new anion-exchange agents from intermediate products of the oxidative degradation of cellulose, e.g., in accordance with the scheme:



Hence, the study of the oxidative degradation of cellulose enables us to obtain a more accurate picture of the chemical processes occurring, to determine their effects on the breakdown of the cellulose molecular chains, and to devise new methods for the investigation of the chemistry of modified celluloses and their applications.

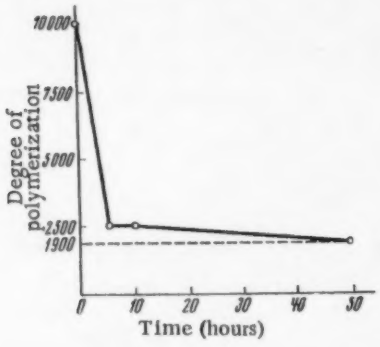


Fig. 5. Change in the degree of polymerization of cellulose heated in a vacuum at 185°.

Investigations into the thermal degradation of cellulose were begun in the Institute of Organic Chemistry of the Academy of Sciences of the USSR and were continued systematically by the Cellulose Chemistry Group of the Forestry Institute of the Academy of Sciences of the USSR. Experiments were carried out in media of nitrogen, argon, air, oxygen, and hydrocarbons, and also in a high vacuum.

As can be seen from Fig. 5, the cellulose molecule has high thermal stability. The sharp fall in degree of polymerization at 185° corresponds to breakdown of weak bonds and consumption of residual adsorbed oxygen in oxidative processes. When this oxygen has been consumed, thermodegradation suffers a sudden check and cannot be detected by viscosity measurements even after five hours' heating. Only after 35 hours can slight degradation be detected. Hence, cellulose is really thermally stable when oxygen is absent from the reaction medium.

Recent results of these investigations have been published [55].

SUMMARY

1. Numerous investigations by various authors have confirmed our early results on the high value of the molecular weight of cellulose.

2. The macromolecular chains of isolated celluloses contain weak links due to the presence of nonglucose units (in the case of wood celluloses) and of glucose units having carboxy and aldehyde groups in positions 2, 3, and 6 which are responsible for various chemical transformations of cellulose in various media.

3. It has been shown that the oxidation reactions of cellulose with oxides of nitrogen, periodic acid, and sodium chlorite are not specific, and a more accurate picture of the chemical transformations of oxycelluloses in acid and alkaline media has been obtained.

4. New ways in which cellulose may be modified have been indicated, and possible applications of oxycelluloses have been pointed out.

5. The complex chemistry of the thermal degradation of cellulose has been somewhat clarified.

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COPOLYMERIZATION OF DIENIC HYDROCARBONS WITH ALKYL VINYL ETHERS

COMMUNICATION 1. EFFECT OF CARBON TETRACHLORIDE ON THE MECHANISM OF THE COPOLYMERIZATION OF BUTADIENE WITH ALKYL VINYL ETHERS

S. N. Ushakov, S. P. Mitsengendler, and V.N. Krasulina

Characteristics of the Butadiene - Alkyl Vinyl Ether System. In the system under investigation, butadiene-alkyl vinyl ether, the two components stand at opposite ends of the series of monomers in average activity. In absence of a polar effect in the system, • a great difference in the activities of the components should not favor copolymerization [1].

In accordance with the modern theory of copolymerization, in such a system butadiene and vinyl ether radicals will react mainly with the active monomer, butadiene; butadiene will therefore predominate in the copolymer. Only increase in the content of inactive component in the original mixture will effect an increase in its content in the copolymer. However, the rate of the process will then be greatly reduced. Unlike inactive vinyl esters, vinyl ethers generally inhibit the polymerization process [1-3]. Some authors [1] consider that the inhibiting effect of vinyl ethers, in particular ethyl vinyl ether, is associated with the activity of the hydrogen of the α-methylene group of the ether and its addition at the initial active centers. The more stable 1-(vinyloxy)ethyl radical is then formed.

In the present paper we describe conditions under which the direction of reaction can be greatly changed, the rate of the copolymerization reaction in the butadiene - alkyl vinyl ether system in presence of benzoyl peroxide being greatly increased. This effect was attained by introduction of carbon tetrachloride into the sphere of reaction. It was shown that in this case two copolymerization mechanisms operate simultaneously and result in the formation of the product of cationic copolymerization, in which the alkyl vinyl ether predominates, and of the product of free-radical polymerization, in which butadiene predominates.

EXPERIMENTAL

Starting Materials. Commercial vinyl ethers (ethyl vinyl and isopropyl vinyl) were purified from alcohols and aldehydes, dried over caustic alkali, and left over sodium [4]. After being fractionated through a 1-meter column, ethyl vinyl ether had b.p. 35.7-35.8°, d_4^{20} 0.759 and n_D^{20} 1.3770, and isopropyl vinyl ether had b.p. 55.6, d_4^{20} 0.755 and n_D^{20} 1.3842. The purity of the ether was checked also by determining its content by the oxime method [4]; the content of $CH_2 = CHOR$ was usually about 99.6%.

Butadiene. Two samples were used. Sample I contained 0.5% of ammonia and butene impurities, and it was purified by washing with 20% sulfuric acid and then water. Sample II contained about 20% of butenes and was purified with the aid of cuprous chloride [5]. The purified butadiene was passed through calcium chloride drying columns. The butadiene content of the material used in the experiments was 99.0-99.5%.

Carbon tetrachloride was purified by treatment with aqueous-alcoholic alkali, washed with water, and dried over calcium chloride. The dried carbon tetrachloride was distilled over paraffin; b.p. 76°.

The active-oxygen content of the benzoyl peroxide was 99.5% of the theoretical amount.

• The two monomers are adjacent in the donor-acceptor series.

Procedure. All experiments were carried out at 65° in an atmosphere of nitrogen or carbon dioxide. At the end of the experiment unchanged butadiene was removed. The polymer was dissolved in benzene and precipitated with a 3- to 5-fold excess of methanol. A soft white elastic copolymer (Fraction I) was precipitated overnight. In experiments with an addition of carbon tetrachloride, after removal of Fraction I a sticky viscous yellow polymer (Fraction II), which was like the polyvinyl ether itself, was slowly precipitated from solution, sometimes only after partial removal of solvents. Both fractions were washed with methanol and dried to constant weight at 50-60° in a vacuum drier. In individual cases the copolymer was fractionated. The content of the ether in the copolymer was determined from the carbon content found by elementary analysis.*

An attempt was made to determine isopropyl vinyl ether directly by a modification of the Zeisel method [6]. However, for polyethers this method is reproducible only within 6-10% and can serve only as a qualitative confirmation of the presence of ether units in the copolymer. The halogen contents of the copolymers were determined by Carius digestion. The unsaturation of the copolymers was determined by the method described by Vasilyev [7].

TABLE 1

Homogeneous Copolymerization of Butadiene with Alkyl Vinyl Ethers in presence of 2-5% of Initiators of the Free-radical Type

Temperature (°C)	Molar ratio ether: butadiene	Initiator	Duration of polymerization (hours)	Yield of copolymer (% by weight)	Butadiene content of copolymer (moles %)	Alkyl vinyl ether
65	1	Benzoyl peroxide	700	11.0	91.5	Isopropyl vinyl ether
80	1	Diazoaminobenzene	160	Traces	—	"
100	1	2,2'-azobis[2-methyl-propionitrile]	278	11.5	95.0	"
100	2		229	6.0	91.5	"
100	4		262	6.7	82.5	"
65	1	Benzoyl peroxide	750	2.5	85.5	Ethyl vinyl ether
65	1	" "	340	Traces	—	"

Homogeneous Copolymerization of Butadiene with Vinyl Ethers. The copolymerization of butadiene with ethyl vinyl and isopropyl vinyl ethers was carried out in presence of various initiators of the free-radical type (benzoyl peroxide, diazoaminobenzene, 2,2'-azobis [2-methylpropionitrile], cumene hydroperoxide) at 65° and 100° with various relative amounts of the vinyl ether and butadiene. In all cases the duration of the process was 400-700 hours and the yield of copolymer of low molecular weight was 2.5-11.5% (Table 1). Butadiene predominated in all the copolymers (up to 95%). With increase in ether concentration to 80% up to 18% of ether units can be introduced into the polybutadiene chain. The results obtained are in full accord with modern views on the activities of the monomers.**

Effect of Carbon Tetrachloride on the Copolymerization of Butadiene with Alkyl Vinyl Ethers in presence of Benzoyl Peroxide. When carbon tetrachloride and benzoyl peroxide were introduced simultaneously into the sphere of reaction, the picture changed sharply. The process proceeded at a considerable rate, even when there was a high concentration of the ether in the original mixture. The higher the concentration of the ether, the more rapid the process. Table 2 illustrates the effect of carbon tetrachloride on the copolymerization of butadiene with isopropyl vinyl ether for a high concentration of the inactive component, isopropyl vinyl ether. Neither benzoyl peroxide alone, nor carbon tetrachloride alone will bring about polymerization. Only when both are present simultaneously will the process proceed at a substantial rate.

* The carbon content of butadiene is 88.9% and that of isopropyl vinyl ether is 69.78%. The difference (19.12%) is such that the composition of the copolymer can be determined accurately within 1%.

** The insignificant variation in the composition of the copolymers, even when the composition of the original mixture was varied greatly, made the determination of the copolymerization constants of the system difficult with the existing method of analysis.

An analogous effect was observed when carbon tetrachloride was added to another initiator, 2,2' - azobis [2-methylpropionitrile]. Addition of 2% of I Br had an effect which was roughly analogous to that of carbon tetrachloride (preliminary experiment).

TABLE 2
Effect of Carbon Tetrachloride and Benzoyl Peroxide on Copolymerization at 65° with a molar ratio ether : butadiene = 4 : 1

Amount (%)		Duration of polymerization (hours)	Yield of polymer (% by weight)
Benzoyl peroxide	Carbon tetrachloride		
2.0	0.0	260	0
0.0	20.0	260	0
2.0	20.0	2.5	66.0

As the extent of transformation increases, the butadiene content of the copolymer increases. Thus, as the progress of copolymerization increases from 25% to 65%, the butadiene content of the product increases correspondingly from 5% to 29% (Table 3).

Analysis of the mean compositions of copolymers obtained over a wide range of ratios of components (Curve 1 in figure) shows that addition of carbon tetrachloride not only accelerates the process, but also effects a great change in the behavior of the monomers in the process: the inactive vinyl ether predominates in the copolymer, and the active monomer, butadiene, contributes only slightly to the composition of the copolymer. Comparison of the composition curves of copolymers obtained in the absence of and in the presence of carbon tetrachloride serves a direct indication that in presence of carbon tetrachloride the process proceeds mainly by a cationic mechanism (see figure) in which the alkyl vinyl ether with its strongly negative C = C link is the active monomer and predominates in the copolymer.

The effect of additions of carbon tetrachloride in the system investigated is analogous to that observed in the copolymerization of alkyl vinyl ethers with chloroprene in presence of benzoyl peroxide alone [8].

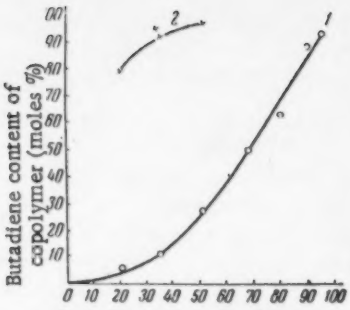
TABLE 3
Effect of Progress of Reaction on the Composition of the Copolymer

Temperature	Composition of original mixture (moles %)		Progress of reaction (%)	Composition of overall product (moles %)	
	Butadiene	Vinyl ether		Butadiene	Vinyl ether
65	50	50	25.0	5	95
65	50	50	64.8	29.0	71

Analysis of Copolymerization Products Obtained in Presence of Carbon Tetrachloride. Investigation of the copolymers obtained showd that they were extremely heterogeneous in composition. When the copolymerization product (a white viscous mass) was reprecipitated with methanol from benzene solution, it was easy to separate it into two fractions, referred to above as Fractions I and II.

Fraction I, like polybutadiene itself, is precipitated from benzene solution by excess of methanol. This is a wide fraction, its butadiene content varying from 15% to 90% and more according to the composition of the original mixture. The fraction containing less than 10-15% of butadiene, like the polyvinyl ether itself, is soluble in methanol and remains in solution; it can be isolated by partial evaporation of solvent. We have called this fraction Fraction II. The butadiene content of Fraction II was generally in the range 1-10%. Table 4 gives the yields and compositions of fractions for original mixtures of various compositions.

With increase in the butadiene content of the original mixture there is an increase also in its content in Fraction I. When the butadiene content of the original mixture is very high, e.g., above 95% the butadiene content of Fraction I exceeds its content in the original mixture and Fraction II is obtained only in traces under these conditions. Thus, increase in the butadiene content increases the relative contribution of the free-radical process. On the other hand, with excess of the ether in the original mixture, it predominates in Fraction I and in the overall product.


Butadiene content of copolymer (moles %)
Butadiene content of original mixture (moles %)
0 10 20 30 40 50 60 70 80 90 100
10 20 30 40 50 60 70 80 90 100
1
2

Relation of the composition of the copolymer to the composition of the original mixture: 1) in presence of carbon tetrachloride; 2) in absence of carbon tetrachloride.

With increase in the contribution of cationic copolymerization, the rate of the overall process increases greatly. Thus it will be seen from Table 4 that a given yield of copolymer of 63-66% can be obtained either with 80% of the ether in the original mixture for 2.5 hours or with 50% of the ether for 56 hours (Experiments 3 and 11).

The observed picture of the copolymerization process, which is characterized by the formation of two fractions of copolymer differing greatly in composition (this being in accord with the free-radical mechanism of copolymerization in the case of one fraction and in accord with the cationic mechanism in the case of the other fraction), gives us grounds to suppose that both these mechanisms operate.

Fractions I and II contained chlorine (1% and 2-3% respectively). The presence of chlorine resulted in a corresponding lowering of the carbon content of the copolymer.*

TABLE 4

Yields and Compositions of the Separate Fractions of the Copolymers

Experiment	Composition of original mixture: Butadiene (moles %)	Composition of original mixture: Vinyl ether (moles %)	Composition of original mixture: Progress of reaction (% by weight)	Duration of reaction (hours)	Yield of Fraction I (%)	Composition of Fraction I: Butadiene (moles %)	Composition of Fraction I: Vinyl ether (moles %)	Yield of Fraction II (% by weight)	Composition of Fraction II: Butadiene (moles %)	Composition of Fraction II: Vinyl ether (moles %)
3	20.0	80.0	66.0	2.5	—	11.4	88.6	26.0		
12	34.4	65.6	68.4	29 0	21.6	28.4	71.6	46.8		
11	50.8	49.2	63.6	56.0	20.0	49.3	50.7	43.6	10.8	89.2
9	67.8	32.2	42.4	108 0	24.0	71.0	29.0	18.4	10.7	89,3
10	79.6	20.4	37.8	108.0	25.2	84.7	15.3	12.6	11,0	89.0
40	89.8	10.2	17.1	42.0	17.1	91.0	9.0	0.0		
41	94.0	6.0	16.4	42.0	16.4	96.0	4.0	0.0		

TABLE 5

Analysis of Butadiene and Vinyl Ether Polymers

Polymer	Content of: Cl (%)	Content of: C (%)	Content of: Theoretical C (%)	Difference in carbon content (%)
Butadiene	0,8	88,04	88,90	0,86
Vinyl ether	2,0	68,35	69,78	1,43

* This fact was taken into account in the calculation of the composition of the copolymers.

Analytical data for butadiene and isopropyl vinyl ether polymers obtained in presence of 20% of carbon tetrachloride and 2% of benzoyl peroxide at 65° are given in Table 5.

TABLE 6

Results of the Fractionation of the Wide Fractions I and II

Fractionation product	Solvent	Precipitant	Content of: Fraction in copolymer (% by weight)	C (%)	Butadiene (moles %)	Chlorine (%)	Unsaturation	Notes
I	Benzene-acetone mixture (60:40) 2% solution of polymer)	[Fraction I]	21.8	83.9	84.0*	1.2	83.2	Soft elastic product
II	Benzene-acetone mixture 60:40) 2% solution of polymer	Methanol	0.3	80.7	57.0			Elastic solid
III			17.2	69.8	15.0	2.7	6.8	
IV	Acetone	[Fraction II]	33.2	67.0	1	3.8	0.3	Fluid polymers
V			20.4	67.0	1	1.1	1.3	
VI	Residue after removal of solvent	Methanol	7.1	67.0	1	—	—	

* We were unable to fractionate this fraction any further.

As will be seen in Table 4, the butadiene content of Fraction II was 10-11%. In several cases the carbon content was 67.5-68%, which corresponds to the composition of the polyether. In such cases we assumed arbitrarily that the butadiene content was 1%, which is within the limits of error of the analysis of the copolymers investigated.

TABLE 7

Results of the Fractionation of Fraction I (mole %)

Fractionation product	Content of fraction (% by weight)	Composition of fraction (mole %): Butadiene	Vinyl ether	Notes
I	60	96.3	3.7	Fraction I
II	9.2	93.7	6.3	
III	30.8	86.1	13.9	

Fractionation of Copolymers. Further fractionation of individual copolymers showed that in copolymerization in equimolecular proportions Fraction I contained not only free-radical copolymer, but also the product of cationic copolymerization enriched in the ether up to 85%. In Table 6 we give the results of such separation of Fractions I and II of copolymers obtained from equimolecular proportions of components at 65° at a progress of reaction of 64-66%.

Table 7 gives the results of the fractionation of Fraction I obtained at a molar ratio butadine : ether of 4 : 1. At this butadiene concentration Fraction I contains only free-radical copolymer. Under these conditions the yield of Fraction II is insignificant.

TABLE 8

Effect of Process Conditions on the Yield of Copolymer

Original mixture (mole %)		Medium	Duration of polymerization (hours)	Progress of reaction (%)
Butadiene	Vinyl ether			
50	50	Dry nitrogen	56.5	63 6
50	50	Dry nitrogen; supplementary drying of butadiene with sodium	351.0	26.0
50	50	Dry carbon dioxide	22	64.2
20	80	Air	41	15.0
20	80	Nitrogen	2.5	66.0

Effect of Conditions Under Which Process is Carried Out. In the course of the investigation it was noted that slight, sometimes inappreciable, changes in conditions effect the rate of the process and the composition of the product. The use of different samples of butadiene, the extent to which it is purified, and the amount of moisture present have great effects on the reproducibility of the results. These conditions have a particularly great effect when the concentration of the ether is high and the contribution of the cationic process is considerable. Factors which favor cationic copolymerization accelerate the overall process, and vice versa.

The presence of traces of moisture or carbon dioxide accelerates the process. On the other hand, exhaustive drying of the butadiene with sodium results in retardation of the process (Table 8).

Our results, of course, enable us to characterize these phenomena only qualitatively.

TABLE 9

Relation of the Variation of Component Ratio during Process to the Initial Concentrations of Components

Molar composition of original mixture		Progress of reaction (%)	Composition of product (mole %)		Initial monomer ratio $\frac{M_1^0}{M_2^0}$	Current monomer ratio $\frac{M_1}{M_2}$
Butadiene (M_1^0), %	Vinyl ether (M_2^0), %		Butadiene	Vinyl ether		
34.4	65.6	68.4	10.7	89.3	0.52	2.80
50.8	49.2	63.6	29.1	70.9	1.04	4.15
67.8	32.2	42.4	51.8	48.2	2.48	3.47
79 6	20.4	37.8	65.6	34.4	6.45	6.79
89.8	10.2	17.1	91.0	9.0	8.90	8.60
94.0	6.0	16.4	96.0	4.0	15.70	14.70

Mutual Effect of the Two Processes. Cationic copolymerization, which results mainly in the consumption of the ether, causes a great increase in the butadiene concentration in the process. Hence, the cationic process itself favors the development of and the increase in the contribution made by free-radical copolymerization, which occurs with excess of butadiene (see above). Whereas the cationic process is associated with preferential consumption of the ether, the free-radical process is associated with preferential consumption of butadiene. As a result, the consumption of monomers in the overall process is more uniform than it would be if the process proceeded by a single mechanism.

The results presented in Table 9 show that with increase in the butadiene content of the initial mixture the initial monomer ratio $\left[\frac{M_1^0}{M_2^0}\right]$ approaches equality with the current ratio $\left[\frac{M_1}{M_2}\right]$ and at a sufficiently high initial butadiene concentration $\left[\frac{M_1^0}{M_2^0}\right] \approx \left[\frac{M_1}{M_2}\right]$ at various stages of the process.

In the copolymerization of the vinyl ether with the nonpolar butadiene, the latter has no effect on the activity of the ether radical.* However, in presence of carbon tetrachloride the activity of the ether may be affected by the positively charged particles (cations) present. The possibility of such an effect can be judged from the work of Hess and Karlin [9], which shows that the addition of Friedel-Crafts catalysts has an appreciable effect on the reactivity of monomers when undergoing free-radical copolymerization.

TABLE 10

Effect of Addition of Carbon Tetrachloride on the Composition of a Free-radical Copolymer obtained from an Equimolecular Mixture of Components

Initiator	Yield of free-radical copolymer (% by weight)	Temperature, °C	Composition of free-radical copolymer (mole %)	
			Butadiene	Vinyl ether
2,2'-Azobis[2-methylpropionitrile]	11.5	100	95.0	5.0
Benzoyl peroxide	24.0	100	75*	25.0*
Benzoyl peroxide + CCl_4	11.0	65	91.5	8.5
Benzoyl peroxide	20.0	65	84.5	15.5

* Fraction with maximum butadiene content

No direct proof was found of such an effect in the present investigation. However, the following facts should be noted: for original mixtures of identical composition, the vinyl ether content of a free-radical copolymer obtained in presence of carbon tetrachloride is greater than that of a copolymer obtained in absence of carbon tetrachloride, although the current vinyl ether concentration is considerably lower in the first case (it is consumed in the cationic process). Thus, for equimolecular concentrations of monomers, the vinyl ether content of the "free-radical" copolymer is 4-8% (Table 1), whereas when carbon tetrachloride is added the vinyl ether content of the copolymer is already 15-25% (Table 10).

As already shown, addition of carbon tetrachloride has a great effect also on the rate of formation of free-radical copolymer. These facts permit us to suppose that the cationic process increases the activity of the vinyl ether in its free-radical copolymerization with butadiene.

Discussion of the Experimental Results. Chalmers [10] showed that alkyl vinyl ethers polymerize very rapidly in presence of a solution of iodine in chloroform with formation of polymers of low molecular weight in accordance with the scheme:

$$CH_2=\underset{\underset{OR}{|}}{CH} + I \rightarrow ICH_2-\underset{\underset{OR}{|}}{CH}-CH_2-\underset{\underset{OR}{|}}{CH}-$$

All the copolymers that we have obtained in presence of the system (benzoyl peroxide + CCl_4) contain chlorine.

For the free-radical mechanism of copolymerization, the presence of chlorine in the copolymers is associated with the known reaction of chain termination by CCl_4 with transfer of the chain to the CCl_3 radical formed. The fact that the cationic product contains chlorine makes it possible to suppose that "Cl" is formed in the system and acts like I_2 as an electrophilic substance allied to Friedel-Crafts catalysts [3]. The fact that traces of moisture accelerate the process permits us to assume that, apart from Cl, HCl formed in presence of CCl_4 is an initiator of cationic copolymerization.**

* This will be seen from data on the compositions of copolymers prepared in absence of carbon tetrachloride.

** Schildknecht states that sometimes contamination with calcium chloride falling from drying tubes or with traces of acidic substances falling from certain types of ceramic fillings for columns is sufficient to initiate the polymerization of alkyl vinyl ethers [3].

The fact, which we have discovered for the first time, of the coexistance of two different processes in one system is interesting also because, when developed, the application of such combined copolymerization may serve as a method for preparing a copolymer of more uniform composition. • This may be attained by the consumption of an extremely inactive component in another process operating in the opposite direction. As they have different properties, the products can always be separated from one another. Removal of excess of the inactive component from the sphere of reaction should also prevent the retardation of the process with time.

SUMMARY

1. For the first time it was shown that it is possible for two different copolymerization mechanisms (free-radical and cationic) to coexist in one system.

2. The relative contributions of the free-radical and cationic processes depend on the initial monomer ratio.

3. In presence of the system (benzoyl peroxide + carbon tetrachloride) the copolymerization of butadiene with an alkyl vinyl ether proceeds largely by the cationic mechanism with formation of copolymers containing 85-99% of the vinyl ether.

4. The occurrence of the cationic process greatly increases the rate of formation of the free-radical copolymer, as compared with the rate of free-radical copolymerization of these components in absence of carbon tetrachloride.

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• We are considering systems of monomers having different activities, in which $r_1 < 1$ and $r_2 > 1$.

MACROMOLECULAR COMPOUNDS

COMMUNICATION 99. POLYCONDENSATION OF DICHLOROMETHANE WITH BENZENE

G. S. Kolesnikov, V.V. Korshak, and T. V. Smirnova

In some previous communications of this series [1-7] we described the results of a study of the polycondensation of 1,2-dichloroethane with benzene and other aromatic hydrocarbons in presence of aluminum chloride. The same subject has been studied also by Klebansky and Mironenko [8], Dolgov and Larin [9], and Shishido and coworkers [10-17]. It is evident from the number of papers that have been devoted to the polycondensation of 1,2-dichloroethane with aromatic hydrocarbons that this reaction has aroused considerable interest.

Very much less attention has been devoted to the interaction of dichloromethane with aromatic hydrocarbons in presence of aluminum chloride, and the polycondensation of dichloromethane with aromatic hydrocarbons has not been studied at all. Friedel and Crafts [18] found that reaction of dichloromethane with benzene in presence of aluminum chloride gave diphenylmethane, anthracene, and toluene; when benzene was replaced by toluene, ditolylmethane, dimethylanthracene, and a mixture of p- and m-xylenes were obtained. Adam [19] treated biphenyl with dichloromethane and obtained fluorene and dibiphenylmethane. Reaction of dichloromethane with 1,2,4-trimethylbenzene gave bis-2,4,5-trimethylphenylmethane [20].

It would be expected that polycondensation of dichloromethane with benzene would proceed as in the polycondensation of 1,2-dichloroethane with benzene, since both dichloromethane and 1,2-dichloroethane contain the same number of halogen atoms capable of reacting with benzene in presence of aluminum chloride. With the object of verifying this supposition, we undertook a study of the polycondensation of dichloromethane with benzene.

EXPERIMENTAL

In the first series of experiments the amounts of benzene and catalyst and the experimental conditions were maintained constant, whereas the amount of dichloromethane was varied. The concentration of the aluminum chloride was 2.25 moles per 100 moles of benzene. The initial bath temperature was 50°; this temperature was maintained for one hour, and the temperature was then raised gradually to 100° over a period of 60-90 minutes. The total period of heating was four hours. Reaction was very vigorous and there was a copious evolution of hydrogen chloride. After the usual treatment [1, 2] diphenylmethane (b.p. 110-120° at 3 mm) and dibenzylbenzene (b. p. 190-210° at 3 mm) were distilled off under reduced pressure. The residue in the flask consisted of poly(methylenephenyl). The molecular weight of the poly(methylenephenyl) was determined viscosimetrically. The results obtained are given in Table 1.

It will be seen from Table 1 that with increase in the dichloromethane : benzene ratio the yield of poly (methylenephenyl) rises a little and the yields of diphenylmethane and dibenzylbenzene fall. Two facts become evident from an examination of the results: constancy of molecular weight and nonformation of three-dimensional polymers at equimolecular ratios and even with an excess of dichloromethane.

As is well known, in the overwhelming majority of polycondensation reactions the molecular weight of the polycondensation products increases as the molar ratio of the reactants approaches unity, and we have shown [1-7] that this rule holds for the polycondensation of 1,2-dichloroethane with benzene and other aromatic hydrocarbons. However, the rule does not hold for the polycondensation of dichloromethane with benzene, the

viscosimetric molecular weight of the resulting poly(methylenephenyl) being almost independent of the relative amounts of reactants.

TABLE 1

Polycondensation of Dichloromethane with Benzene

Molar ratio dichloromethane : benzene	Yield (% on dichloromethane taken)			Molecular weight of poly(methylenephenyl)
	Diphenylmethane	Dibenzylbenzene	poly(methylenephenyl)	
0.50	21.4	13.2	21.6	1370
0.59	18.0	11.6	26.4	1180
0.65	15.7	10.6	24.8	970
0.70	14.4	10.8	27.4	1400
0.75	13.2	11.3	29.5	1280
0.83	10.9	9.5	27.4	1470
0.90	11.0	9.0	28.3	1180
1.00	9.2	7.1	26.1	1100
1.10	8.8*	6.7*	29.8*	1360

* Yield as % on benzene taken.

The above-noted peculiarities of the polycondensation of dichloromethane with benzene can, in our opinion, be explained as follows. This polycondensation can be represented by the scheme:

$$C_6H_6 + CH_2Cl_2 + C_6H_6 \xrightarrow{AlCl_3} C_6H_5CH_2C_6H_5 + 2HCl.$$

$$C_6H_5CH_2C_6H_5 + CH_2Cl_2 + C_6H_6 \xrightarrow{AlCl_3} C_6H_5CH_2C_6H_4CH_2C_6H_5 + 2HCl \text{ etc.}$$

or in a general form:

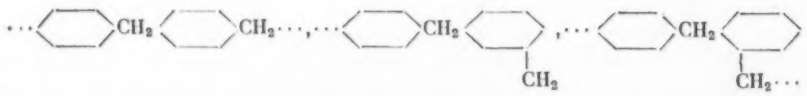
$$(n+1)\,C_6H_6 + nCH_2Cl_2 \xrightarrow{AlCl_3} H(C_6H_4CH_2)_n C_6H_5 + 2n\,HCl.$$

We did not observe the formation of compounds containing a terminal CH_2Cl group, and even when the polycondensation was carried out with excess of dichloromethane the product did not contain chlorine.

The fundamental repeating unit in the linear polycondensation product from dichloromethane and benzene is the group $-C_6H_4CH_2-$, and it may therefore be called poly(methylenephenyl). Elementary analysis showed that the carbon and hydrogen contents of poly(methylenephenyl) obtained from a mixture containing excess of benzene are in close agreement with the values calculated for the repeating unit $-C_6H_4CH_2-$:

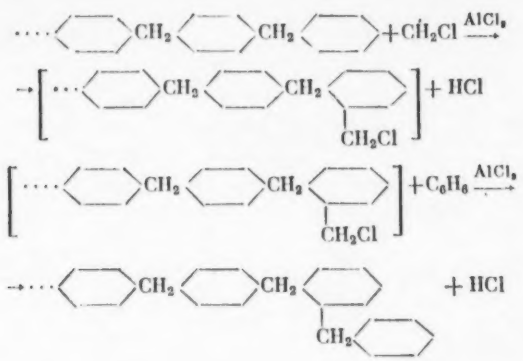
Found %: C 93.07; 93.40; H 6.73; 6.68 C_7H_6. Calculated %: C 93.29; H 6.71

During chain growth new methylene groups may enter not only para and meta positions, as indicated by the low-molecular-weight polycondensation products, but also in ortho positions to methylene groups already present, i.e., the following structural fragments are possible:

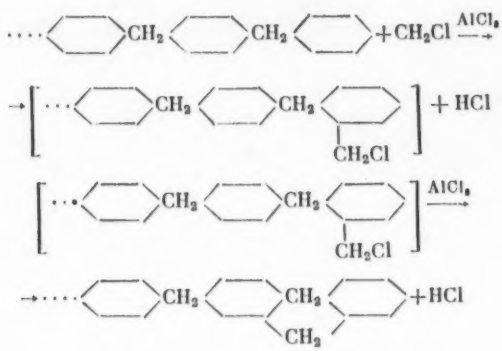


Chain growth is not hindered by para and meta substitution, but this cannot be said of ortho substitution.

In the case of ortho substitution two competing reactions may occur - chain growth, i.e.,



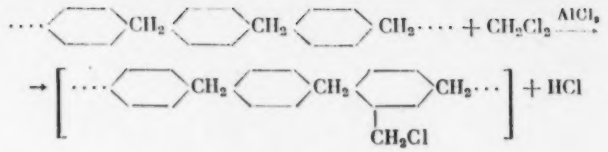
and intramolecular cyclization with formation of a dihydroanthracene residue, i.e.,



We consider that intramolecular cyclization will occur more readily, since, unlike the chain-growth reaction, it does not depend on the occurrence of a collision between molecules of a definite type. The formation of dihydroanthracene ring systems at the ends of growing chains leads to arrest of polymer chain growth, since the alkylation of anthracene and of dihydroanthracene does not occur readily [21]. It would appear that the probability of ortho substitution in the reaction of dichloromethane with benzene in presence of aluminum chloride is independent of the relative amounts of reactants, within the limits indicated in Table 1, so that condensation products of the same chain length are formed in all cases. The formation of terminal dihydroanthracene residues was noted by one of us together with Lebedev and Tsipershtein [22] in the polycondensation of benzyl chloride. In the opinion of the authors, the cause of the arrest in chain growth is the formation of dihydroanthracene end groups.

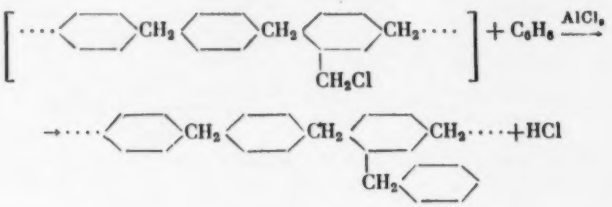
Nonformation of insoluble three-dimensional polycondensation products in the reaction of dichloromethane with benzene may be explained as follows. The formation of three-dimensional products must be preceded by the formation of branched molecules by reaction between linear polymer molecules, dichloromethane, and benzene. The main type of substitution in the polycondensation of dichloromethane with benzene is para substitution. This assertion is based, first, on the fact that the main low-molecular-weight condensation product formed in the early stages of the process is p-dibenzylbenzene and, second, on the analogy shown with the polycondensation of 1,2-dichloroethane with benzene [1,2].

Hence, the formation of branched poly(methylenephenyl) molecules can result from the entry of new methylene groups, and in the great majority of cases these groups will enter positions ortho to existing methylene groups.

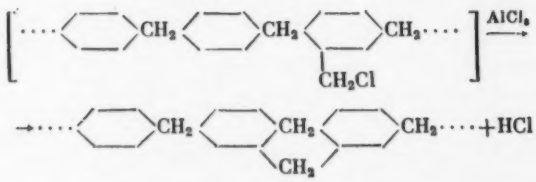


These are two possible ways in which reaction may proceed:

1) Reaction of the chloromethyl group with benzene and formation of a branch chain, i.e.,



2) Reaction of the chloromethyl group with the neighboring aromatic nucleus and formation of a dihydroanthracene ring system, i.e.,



In our opinion the second way is the more probable, since in this case reaction occurs within the molecule and does not require a collision of the molecule of the intermediate compound with a molecule of benzene or any other molecule of aromatic character.

If this explanation is correct, then we may expect nonformation of three-dimensional polycondensation products even when the amount of dichloromethane is greatly in excess of the equimolecular amount. Experiments designed to verify this suggestion and to determine the effect of the concentration of catalyst showed that no three-dimensional products are formed even when the dichloromethane : benzene ratio is 1.5 : 1; at a ratio of 2 : 1 three-dimensional products are formed only at high concentrations of catalyst, and the amount of such product then formed is not great. The results of these experiments are given in Tables 2-4; the experimental conditions were as indicated above. It was found also that, when the dichloromethane : benzene ratio was raised to 3.12 : 1 at an aluminum chloride concentration of 4.3 moles per 100 moles of dichloromethane, the yield of poly(methylenephenyl) was 64.9% (molecular weight 2970) and no three-dimensional products were formed.

It will be seen from Tables 2-4 that increase in the concentration of catalyst results in an increase in the yield of poly(methylenephenyl) and an increase also in its molecular weight; formation of three-dimensional products is accompanied by reduction in the molecular weight of the poly(methylenephenyl).

The products of the initial stage of the polycondensation of dichloromethane and benzene are diphenylmethane and a mixture of p- and m-dibenzylbenzenes with a prepondérance of the para isomer. Diphenylmethane was identified by its melting and boiling points, and it was also oxidized to benzophenone, which showed no depression of melting point in admixture with pure benzophenone. The mixture of dibenzylbenzenes was separated into solid and liquid fractions. The solid was crystallized from alcohol and then melted at 85-86°; the literature [23] gives 85-87.5° for the melting point of p-dibenzylbenzene. Oxidation of the solid with

TABLE 2

Polycondensation of Dichloromethane with Benzene
(dichloromethane : benzene = 1.00)

Catalyst conc. (moles/100 moles of dichloromethane)	Yield (%)			Molecular wt. of poly (methylenephenyl)
	Diphenylmethane	Dibenzylbenzene	Poly(methylenephenyl)	
2.25	9.2	7.1	26.1	1100
4.50	7.2	6.7	37.6	1710
6.75	7.9	6.2	36.7	1570
9.00	6.7	5.3	37.8	1650
11.25	6.8	2.7	40.2	1820
15.00	5.2	1.6	45.0	2090

TABLE 3

Polycondensation of Dichloromethane with Benzene
(dichloromethane : benzene = 1.50)

Catalyst conc. (moles/100 moles of dichloromethane)	Yield (% on benzene taken)			Molecular wt. of poly (methylenephenyl)
	Diphenylmethane	Dibenzylbenzene	Poly(methylenephenyl)	
1.50	15.3	5.8	3.9	1020
3.0	16.4	10.7	34.2	1130
6.0	8.1	5.1	43.4	2170
9.0	6.2	3.7	48.1	1940

TABLE 4

Polycondensation of Dichloromethane with Benzene
(dichloromethane : benzene = 2.00)

Catalyst conc. (moles/100 moles of dichloromethane)	Yield (% on benzene taken)			Molecular wt. of poly (methylenephenyl)
	Diphenylmethane	Dibenzylbenzene	Poly(methylenephenyl)	
1.12	20.7	6.3	5.6	1650
2.25	13.6	4.2	53.6	1710
4.50	7.4	2.8	60.9	2180
6.75	6.7	2.1	63.5*	2130
9.00	3.3	—	49.5**	1820

* Including 1.2% of three-dimensional polymer.

** Including 5% of three-dimensional polymer.

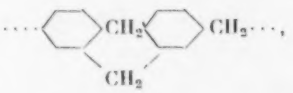
chromium trioxide gave p-dibenzoylbenzene, m.p. 160-161°, identical with the value for p-dibenzoylbenzene in the literature [24, 25].

Found %: C 84.51; 84.34; H 4.70; 4.68 $C_{20}H_{14}O_2$. Calculated %: C 83.88; H 4.89

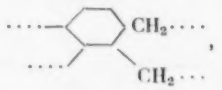
The liquid product was redistilled under reduced pressure and a fraction of b.p. 249-250° (26 mm) was collected. This fraction did not solidify when distilled again, and it was oxidized with chromium trioxide with formation

of m-dibenzoylbenzene, m.p. 98-99° (from alcohol); the literature gives 99.5-100° for the melting point of m-dibenzoylbenzene [24, 26].

If the above suggestion concerning the formation of dihydroanthracene ring systems in the poly(methylenephenyl) chain and at its end is correct, then this fact should be reflected in the composition of the polycondensation products as expressed by the carbon : hydrogen ratio. When dihydroanthracene residues are completely absent in the polymer, this ratio should be 13.9, and if the polymer chain consists entirely of dihydroanthracene residues linked through methylene groups, i.e.,

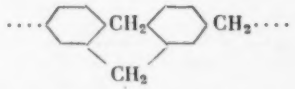


then the carbon : hydrogen ratio should be 14.9. With the maximum possible number of methylene bridges, i.e., when the polycondensation product consists of the units



this ratio should be 15.9.

In order to verify this suggestion we subjected some samples of poly(methylenephenyl) to extraction treatments in order to resolve them into poly(methylenephenyl) soluble in hot alcohol (Fraction I) and of relatively low molecular weight and poly(methylenephenyl) that is insoluble in hot alcohol (Fraction II) and of higher molecular weight. Fractions I and II were analyzed for carbon and hydrogen, and it was found that Fraction II was always richer in carbon than Fraction I. The C: H ratios in Fractions I and II were, respectively, 13.7 and 14.9 for one sample of poly(methylenephenyl) and 13.9 and 14.3 for another. The C: H ratio of Fraction I was close to the ratio calculated for a repeating unit of $-C_6H_4CH_2-$, and that of Fraction II was higher and attained the value calculated for the repeating unit



On the basis of these results we may conclude that the poly(methylenephenyl) obtained by the polycondensation of dichloromethane with benzene in presence of aluminum chloride contains fractions that are richer in carbon than would be expected for poly(methylenephenyl) containing only the repeating unit $-C_6H_4CH_2-$. The high carbon content may be the result of the presence of dihydroanthracene residues in the poly(methylenephenyl) molecule.

The presence of hydroaromatic rings in poly(methylenephenyl) was proved by dehydrogenation of the poly(methylenephenyl) with selenium. It is known that only cycloparaffins are dehydrogenated by selenium, aromatic compounds being formed in the case of six-membered rings [27, 28]. Dehydrogenation of poly(methylenephenyl) with selenium gave a product having a C : H ratio of 15.4, whereas the ratio was 14.3 for the fraction of the original poly(methylenephenyl) that was insoluble in hot alcohol. It was proved, therefore, that poly-(methylenephenyl) contains hydroaromatic rings, and in our opinion such rings can only be those of dihydroanthracene residues; we consider that it is scarcely possible that hydroaromatic rings of any other type could be formed.

Poly(methylenephenyl) is a thermally stable substance and can be heated in absence of air to 380-400° without appreciable change. After one hour at this temperature at a residual pressure of 3 mm the polymer showed no appreciable change in molecular weight. Heating to a higher temperature at atmospheric pressure results in pyrolysis, and from the pyrolysis products anthracene was isolated and identified by its melting point, absence of depression of melting point in a mixture test, and results of elementary analysis.

As catalyst for the polycondensation of dichloromethane with benzene, not only aluminum chloride, but also anhydrous ferric chloride, zirconium chloride, and aluminum bromide were tried. The results of these experiments, which were of an exploratory character, are given in Table 5; in all experiments the catalyst concentration was 3.00 moles per 100 moles of benzene and the benzene : dichloromethane ratio was 1.4.

TABLE 5

Polycondensation of Dichloromethane with Benzene

Catalyst	Yield (%)			Molecular wt. of poly (methylene-phenyl)
	Diphenyl-methane	Dibenzyl-benzene	Poly (methylene-phenyl)	
$AlCl_3$	12.1	9.3	24.0	1290
$FeCl_3$	—	—	—	—
$ZrCl_4$	3.1	—	—	—
$AlBr_3$	10.8	3.1	17.3	2170

It will be seen from Table 5 that ferric chloride is not a catalyst for the polycondensation of dichloromethane with benzene and zirconium chloride is a very feeble catalyst for this reaction.

SUMMARY

1. A study was made of the polycondensation of dichloromethane with benzene in presence of aluminum chloride.

2. It was shown that in the polycondensation of dichloromethane with benzene a polymer is formed which contains dihydroanthracene residues. The presence of these residues in the polymer chain results in the arrest of chain growth and hinders the formation of branched and three-dimensional polymers.

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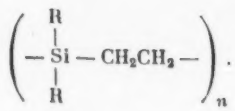
BRIEF COMMUNICATIONS

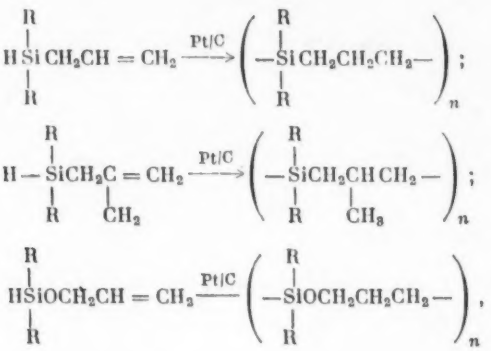
SYNTHESIS AND POLYMERIZATION OF COMPOUNDS IN WHICH HYDROGEN AND AN UNSATURATED RADICAL ARE ATTACHED TO SILICON

V. F. Mironov and A. D. Petrov

Until recently work on the polymerization of unsaturated silahydrocarbons has yielded only polymers in which the silicon atoms are in side chains [1]. In 1956 Curry [2] found that, when silahydrocarbons in which hydrogen and a vinyl radical are attached to silicon are heated in presence of a catalyst (platinized charcoal), polymers are formed of the following type:



In the present investigation we found that allyl-, 2-methylallyl-, and allyloxy-silanes containing silicon-attached hydrogen readily form similar polymers with silicon atoms in the polymer chain:



in which R = Cl, CH_3, C_2H_5, and C_6H_5.

These compounds are readily accessible, for the allyl - and 2-methylallyl-dichlorosilanes required for their preparation are formed in predominant amounts in the direct synthesis under the conditions that we have found. The properties of the compounds synthesized for the first time are given in the table.

EXPERIMENTAL

Allyldichlorosilane $CH_2=CHCH_2SiHCl_2$

A glass tube, length 580 mm and diameter 38 mm, was filled rather loosely with pieces (20 × 20 × 20 mm, approximately) of 80 : 20 silicon-copper alloy. The tube was heated at 300 ± 10° in an electric tube furnace,

and allyl chloride was passed into the tube at a rate of 60 drops per minute. From 2 kg of allyl chloride, 1310 g of condensate was obtained, and distillation through a column gave 356 g of allyldichlorosilane, 185 g of $CH_2=CHCH_2SiCl_3$, and 103 g of $(CH_2=CHCH_2)_2SiCl_2$. The total yield of allylchlorosilanes was 49% on the amount of condensate, and they were obtained in the proportions 1 : 0.5 : 0.3. The literature [3] states that the yield is 60% and $C_3H_5SiCl_3$ predominates.

No.	Formula of compound	B. p. (°C)	p (mm)	n_D^{20}	d_4^{20}
1	$(CH_3)_2HSiCH_2CH=CH_2$	69	(755)	1.4075	0.7086
2	$(C_2H_5)_2HSiCH_2CH=CH_2$	127.8	(745)	1.4330	0.7580
3	$(C_6H_5)_2HSiCH_2CH=CH_2$	155	(10)	1.5760	1.0000
4	$(C_6H_5)(CH_3)HSiCH_2CH=CH_2$	76	(8)	1.5137	0.8937
5	$(C_2H_5O)_2HSiCH_2CH=CH_2$	54	(22)	1.4063	0.8607
6	$(C_6H_5)CH_3HSiOCH_2CH=CH_2$	83	(7)	1.4955	0.9455
7	$(C_2H_5)_2HSiOCH_2CH=CH_2$	55	(40)	1.4175	0.8174
8	$CH_3HSi(OCH_2CH=CH_2)_2$	43	(15)	1.4159	0.8852
9	$(CH_3)_2Si(OCH_2CH=CH_2)_2$	155.8	(745)	1.4170	0.8822
10	$(C_2H_5)_2Si(OCH_2CH=CH_2)_2$	72	(7)	1.4302	0.8888
11	$(C_6H_5)_2HSiCH_3$	93.5	(1)	1.5717	0.9945
12	$(C_6H_5)_2HSiC_2H_5$	119.8	(1)	1.5674	0.9900

Dichloro(2-methylallyl)silane $CH_2=C(CH_3)-CH_2SiHCl_2$

Treatment of 613 g of 2-methylallyl chloride under similar conditions gave 543 g of condensate, and from this we isolated 133 g of $C_4H_7SiHCl_2$, b.p. 115-118°, 110 g of $C_4H_7SiCl_3$, b.p. 135-137°, and 45 g of $(C_4H_7)_2SiCl_2$, b.p. 203-210°. The yield of chloro(2-methylallyl)silanes was 53.5%, and they were obtained in the proportions 1 : 0.8 : 0.3. When the rate of passage of 2-methylallyl chloride was doubled, the proportions of chloro(2-methylallyl) silanes were 1 : 1.2 : 0.4. The literature [4] states that the yield is 40% and the proportions are 1 : 1.8 : : 0.45.

Allyldiethylsilane $CH_2=CHCH_2SiH(C_2H_5)_2$

A solution of 70 g of $Cl_2HSiC_3H_5$ in an equal volume of ether was added to a cooled solution of ethylmagnesium bromide prepared from 24 g of magnesium and 120 g of ethyl bromide in 500 ml of ether. On the next day the contents of the flask were boiled for five hours and then decomposed by water. The ether layer and ether extracts of the aqueous layer were dried with calcium chloride. Ether was distilled off, and distillation of the liquid residue through a column gave 39 g of $C_3H_5SiH(C_2H_5)_2$, b.p. 127-129° (yield 61%). Compounds No. 1, 3 and 4 in the table were synthesized under similar conditions.

(Allyloxy)diethylsilane $CH_2=CHCH_2OSiH(C_2H_5)_2$

To a stirred mixture of 250 ml of ether, 50 g of pyridine, and 40 g of allyl alcohol, 67 g of $(C_2H_5)_2SiHCl$ was added. On the next day the pyridine salt was filtered off and washed with ether. Ether was distilled from the filtrate, and the liquid residue was vacuum-distilled; it gave 42 g (53%) of $C_3H_5OSiH(C_2H_5)_2$, b.p. 53-56°. Compounds No. 5-10 were synthesized under similar conditions.

Ethyldiphenylsilane $C_2H_5(C_6H_5)_2SiH$

Dichloroethylsilane (64.6 g) was added to phenylmagnesium bromide prepared in 400 ml of ether from 24.3 g of magnesium and 185 g of bromobenzene. The contents of the flask were boiled for four hours, and on the next day they were decomposed with water. The usual treatment gave 95.3 g (90%) of ethyldiphenylsilane, b.p. 118-120° (1 mm). Methyldiphenylsilane was prepared similarly.

Polymerization of Alkenylsilanes

1) Allyldichlorosilane (14 g) was boiled in presence of 0.05 g of platinized charcoal (15% Pt). After ten minutes the boiling point rose from 97° to 110°, and after a further ten minutes it attained 300°. In the course

of four hours at 300° no boiling and no decomposition were observed. It is interesting to note that Wagner [5] obtained a liquid polymer from dichlorovinylsilane.

2) A mixture of 14.5 g of allyldiethylsilane and 0.02 g of platinized charcoal was boiled for four hours; the boiling point rose by 20°. After a break of two days it was found that the boiling point had become 180°, and in ten minutes' boiling it attained 300°. A clear viscous liquid was obtained.

3) Allyldiphenylsilane (14.2 g) was boiled for five hours under the conditions indicated. An extremely viscous mass was obtained.

4) Under the same conditions, allyldimethylsilane did not polymerize. Curry [2] found that the extent of polymerization of dimethylvinylsilane was even greater than that of diethylvinylsilane.

5) (Allyloxy)diethylsilane polymerized after two hours at the boiling point.

TABLE

MR		Yield	Found (%)			Calculated (%)		
Found	Calc.	(%)	C	H	Si	C	H	Si
34.86	34.88	48	59.93; 59.87	12.12; 12.12	28.40; 28.49	59.91	12.06	28.02
43.99	43.90	61	65.70; 65.68	12.52; 12.50	22.16; 21.17	65.53	12.57	21.89
74.20	74.52	46.7	—	—	12.22; 12.29	—	—	12.51
54.65	54.70	85	—	—	—	—	—	—
45.75	45.66	70	—	—	—	—	—	—
55.04	55.28	62	—	—	—	—	—	—
44.44	44.48	53	60.02; 59.84	10.06; 10.22	14.35; 14.08	59.94	10.06	14.01
44.86	45.01	65	53.45; 53.20	9.00; 9.11	17.80; 17.85	53.11	8.91	17.74
49.12	49.38	85	56.09; 55.79	9.38; 9.46	16.22; 15.93	55.76	9.36	16.30
58.26	58.40	74	58.34; 58.10	11.15; 11.02	19.55; 19.58	58.26	11.17	19.46
65.55	65.58	60.6	78.73; 78.48	7.03; 7.07	14.09; 13.78	78.73	7.11	14.15
70.10	70.14	90	78.93; 79.00	7.60; 7.83	13.50; 13.35	79.17	7.59	13.22

SUMMARY

Allyl-, 2-methylallyl-, and allyloxy-silanes containing silicon-attached hydrogen were synthesized for the first time and polymerized with formation of polymers having silicon atoms in the main chain.

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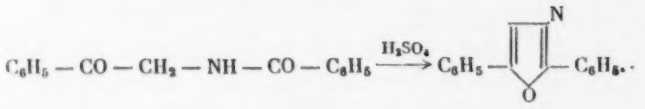
PREPARATION OF 2,5-DIPHENYLOXAZOLE AND ITS SCINTILLATION EFFICIENCY IN PLASTICS

N. A. Adrova, M. M. Koton, and F. S. Florinsky

2, 5-Diphenyloxale has received much practical application in scintillation counters for the recording of radioactive radiations. Various methods of preparing 2,5-diphenyloxazole are indicated in the literature [1]. We selected a method [2] permitting the preparation of a substance of high purity, which is very important for spectroscopic purposes. As our starting material for the synthesis we used 2-aminoacetophenone hydrochloride, which was converted into the benzoyl derivative, N-phenacylbenzamide, and then cyclized by Robinson's method with concentrated sulfuric acid:



EXPERIMENTAL

The synthesis of 2,5-diphenyloxazole was carried out in three stages: 1) preparation of 2-aminoacetophenone hydrochloride; 2) preparation of N-phenacylbenzamide; and 3) cyclization with formation of 2,5-diphenyloxazole.

Hexamethylenetetramine (14.2 g) was added to a solution of 20 g of 2-bromoacetophenone in 200 ml of chloroform. The addition product formed by 2-bromoacetophenone with hexamethylenetetramine appeared immediately as a white crystalline precipitate:

$$R - CO - CH_2Br + N_4(CH_2)_6 \rightarrow R - CO - CH_2 - [N_4(CH_2)_6]\,Br.$$

On the next day the precipitate was filtered off, washed with chloroform, and dried in the air. The product, m.p. 165°, was obtained in 80% yield on the amount of 2-bromoacetophenone taken.

2-Aminoacetophenone Hydrochloride was prepared by acid hydrolysis of the addition product formed by 2-bromoacetophenone with hexamethylenetetramine [3]. This addition product (43 g) was introduced into a round-bottomed flask fitted with mechanical stirrer and reflux condenser, and a solution of 37 ml of 38% hydrochloric acid in 290 ml of alcohol was added. The mixture was allowed to stand for three days at room temperature with intermittent stirring. The precipitated ammonium chloride was filtered off, and the filtrate was vacuum-distilled. The residue from the distillation was dried and recrystallized from alcohol in presence of active charcoal. The resulting 2-aminoacetophenone hydrochloride (18 g) was a white crystalline substance, m.p. 192°, and readily soluble in water.

N-Phenacylbenzamide [4] was prepared as follows. Anhydrous sodium acetate (3.5 g) was added to a solution of 7 g of 2-aminoacetophenone hydrochloride in 35 ml of glacial acetic acid; 7 g of benzoyl chloride was added dropwise, and a further 3.5 g of sodium acetate was then added. The mixture was heated in a water bath for ten minutes and was then poured into 350 ml of water. The precipitated crystals were filtered off and recrystallized from 30 ml of alcohol. The yield of N-phenacylbenzamide, m.p. 122°, was 4.4 g.

2,5-Diphenyloxazole was prepared as follows. A solution of 1 g of N-phenacylbenzamide in 5 ml of concentrated sulfuric acid was heated for two minutes in a boiling water bath and then poured into water. The precipitated crystals were filtered off, dried in the air, and dissolved in benzene. The benzene solution was passed through a column of activated alumina. Benzene was distilled off under reduced pressure, and the 2,5-diphenyloxazole was recrystallized from petroleum ether. 2,5-Diphenyloxazole, m.p. 71-72°, is a white crystalline substance which fluoresces strongly in ultraviolet radiation. For the preparation of efficient scintillating plastics we selected the concentration of 2,5-diphenyloxazole at which the highest relative impulse frequency was observed (see table).

TABLE

Effect of Concentration of 2,5-Diphenyloxazole on the Scintillation Properties of Polystyrene

Concentration of 2,5-diphenyloxazole	Relative impulse frequency (%) *	Concentration of 2,5-diphenyloxazole	Relative impulse frequency (%) *
0.001	20	1.500	106
0.010	30	2.000	103
0.100	55	3.000	103
0.300	86	4.000	92
1.00	106—118		

* With respect to stand.sample (2% of terphenyl in polystyrene)

Preparation of Scintillating Plastic Composition. A mixture of carefully purified styrene monomer, 1% on its weight of 2,5-diphenyloxazole, and 0.20% on its weight of purified benzoyl peroxide was prepared in glass ampoules. The substances dissolved in the styrene at room temperature. The ampoules were cooled thoroughly to prevent vaporization of styrene monomer and repeatedly evacuated; they were then sealed, and the temperature was raised gradually to effect polymerization: 90° for 24 hours, 100° for 72 hours, 110° for 24 hours, and 120° for six hours. The thermostat was then switched off, and the ampoules cooled slowly. The products broke away from the glass, which cracked. The transparent block obtained was annealed to remove strains. It was readily worked on the lathe to the desired size and form.

SUMMARY

1. A method was developed for the synthesis of very pure 2,5-diphenyloxazole.

2. A method is described for the introduction of 2,5-diphenyloxazole into polystyrene in order to give plastics of high scintillation efficiency.

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IONIC AND FREE-RADICAL POLYMERIZATION AND COPOLYMERIZATION OF VINYL ETHERS OF CYCLOHEXANOL, DECAHYDRO-2-NAPHTHOL, AND 2-NAPHTHOL

A. V. Bogdanova, M. F. Shostakovsky, and G. K. Krasilnikova

The study of the polymerization and copolymerization of vinyl ethers containing cyclohexyl, decahydro-2-naphthyl, and 2-naphthyl radicals is of interest both from the point of view of a comparison of the properties of these compounds and also from the point of view of preparing practically useful products from them. As we have previously studied the polymerization and copolymerization of phenyl vinyl ether and, to some extent, cyclohexyl vinyl ether [1-4], it has now become possible to compare the reactivities of vinyl ethers in which the second radical is saturated with the ethers containing the corresponding unsaturated radicals. However, no systematic investigation has yet been made into the conditions of polymerization and copolymerization of cyclohexyl, decahydro-2-naphthyl, and 2-naphthyl vinyl ethers in presence of boron trifluoride, benzoyl peroxide, or 2,2'- azobis [2-methylpropionitrile]. Nevertheless, some polymers and copolymers of decahydro-2-naphthyl and cyclohexyl vinyl ethers have already found application in technology [5, 6], which makes further research in this direction desirable.

The polymerization and copolymerization of these ethers were studied under the conditions required for the ionic and for the free-radical mechanisms. We effected ionic polymerization and copolymerization in presence of boron trifluoride. In this case it may be assumed that, in presence of traces of moisture, the complex $H^+[BF_3 \cdot OH]^-$ is formed [7] and this brings about the liberation of a carbonium ion:

$$CH_2 = CH - OR \cdots H(BF_3 \cdot OH) \longrightarrow CH_3 - \overset{+}{C}H - OR + (BF_3 \cdot OH)^-$$

Free-radical polymerization and copolymerization of these ethers were effected with the aid of benzoyl peroxide, with the aid of 2,2' -azobis [2-methylpropionitrile], and by heat alone. In this case the initiators of polymerization were free radicals formed in the primary breakdown of benzoyl peroxide [8, 4] and 2,2' -azobis 2-methylpropionitrile] [3, 8]. The main part in the development and growth of the polymer chain was played by complex radicals formed by reaction of products of the breakdown of the initiator with a monomer molecule. An interesting peculiarity of aryl and perhydroaryl vinyl ethers is that, unlike alkyl vinyl ethers, they generally give solid polymers.

A comparative study of the conditions required for polymerization and copolymerization and also of the compositions of the copolymers obtained enables us to place the vinyl ethers investigated in the following series, representing their relative reactivities in these processes: butyl vinyl > decahydro-2-naphthyl vinyl > cyclohexyl vinyl > phenyl vinyl > 2-naphthyl vinyl.

EXPERIMENTAL

The ionic polymerization of 2-naphthyl vinyl, decahydro-2-naphthyl vinyl, and cyclohexyl vinyl ethers was carried out in a flask fitted with stirrer. A few drops of a 5% solution of the ether complex of boron trifluoride in ether were added to the vinyl ether at room temperature, and the temperature of the mixture rose to 110-130°. The product was dissolved in ether, the catalyst was neutralized with potassium carbonate, and the

polymer was reprecipitated with methanol. The polymer was vacuum-dried to constant weight and characterized. The yield of polymer was 80-96%. The polymers ranged in molecular weight from 500 to 2000; they were all white or slightly yellowish products, soluble in ether, benzene, and dioxane, but insoluble in alcohols. Polymerized decahydro-2-naphthyl vinyl ether is insoluble in petroleum ether and gasoline.

In the ionic copolymerization of the vinyl ethers studied, the catalyst was boron trifluoride and ethyl vinyl, butyl vinyl, and phenyl vinyl ethers were used as second components. Six pairs of vinyl ethers were taken in various molecular proportions. The procedure and method of isolating the copolymers did not differ from those described above for polymerization. The copolymers obtained were viscous liquids and solids; they were colorless or faintly yellow (naphthyl vinyl and phenyl vinyl ethers). For the characteristics of the copolymers see Table 1.

TABLE 1

No.	Vinyl ethers	Molar ratio of vinyl ethers	Molecular weight of copolymer	Yield of copolymer (%)	Ratio of monomers in copolymer (mole %)
1	Cyclohexyl vinyl ether + butyl vinyl ether	1 : 1	1653.0	79 0	36.7 : 63.3
2	Cyclohexyl vinyl ether + phenyl vinyl ether	1 : 1	1060.0	60.7	76.06 : 12.5
3	2-Naphthyl vinyl ether + ethyl vinyl ether	1 : 1	1142.0	31.0	17.8 : 82.2
4	Ditto	1 : 2	1309.0	48 0	2.60 : 97.4
5	2-Naphthyl vinyl ether + phenyl vinyl ether	1 : 2	597.0	41.0	37.6 : 62.4
6	Decahydro-2-naphthyl vinyl ether + butyl butyl vinyl ether	1 : 1	2118.0	—	38.1 : 61.9

The conditions for polymerization with the aid of benzoyl peroxide, with the aid of 2,2' -azobis [2-methylpropionitrile], and by heat alone were studied for cyclohexyl vinyl, decahydro-2-naphthyl vinyl, and 2-naphtyl vinyl ethers, the reactions being carried out in sealed tubes. Colorless solid polymers (molecular weight 1000-1600) of 2-naphthyl vinyl and decahydro-2-naphthyl vinyl ethers were obtained by heating the monomers with 3-5% of 2,2' -azobis [2-methylpropionitrile] at 60° for 100 hours. Monomer was removed from the crude polymer by treatment with steam, and the residue was reprecipitated from ether solution with methanol and vacuum-dried to constant weight. The polymers obtained contained nitrogen. Polymerization of cyclohexyl vinyl and decahydro-2-naphthyl vinyl ethers in presence of 5% of benzoyl peroxide was carried out at 80-90° for five

TABLE 2

No.	Reactants	Molar ratio of reactants	Yield of copolymer (% on original mixture)	Ratio of monomers in copolymer (mole %)	Molecular weight of copolymer
1	Cyclohexyl vinyl ether + methyl methacrylate	1 : 3	80	14.3 : 85.7	3318
2		1 : 1	52	22.4 : 77.6	2734
3		3 : 1	26	30.6 : 69.4	2343
4	Cyclohexyl vinyl ether + methyl acrylate	1 ; 3	32	16.24 : 83.76	1741
5		1 : 1	25	31.2 : 69.8	2953
6		3 : 1	28	40.8 : 59,2	4124
7	Decahydro-2-naphthyl vinyl ether + methyl methacrylate	1 : 3	66.0	10.9 : 89,1	1798
8		1 : 1	38.5	21.4 : 78.6	2283
9		3 : 1	21.0	31.4 : 68.6	1943
10	Decahydro-2-naphthyl vinyl ether + methyl acrylate	1 : 3	74.0	19.8 : 80,2	5007
11		1 : 1	42.0	36,0 : 64,0	1628
12		3 : 1	22.00	44.0 : 56.0	2493
13	Phenyl vinyl ether + methyl methacrylate	1 : 3	78.2	9.82 : 90.18	2818
14		1 : 1	54.6	14.9 : 85,1	3213
15	Phenyl vinyl ether + methyl acrylate	1 : 3	54.0	15.4 : 84.6	3757
16		1 : 1	45.3	24.4 : 75.6	2539
17		3 : 1	41.0	30.9 : 69.1	3367

hours; colorless solid polymers were obtained in 70% yield. Reduction in the amount of benzoyl peroxide reduced the yield of polymers considerably. When cyclohexyl vinyl ether was boiled for a long time in absence of an initiator, a solid polymer was obtained in 10% yield.

Investigation of the conditions of copolymerization of the vinyl ethers with methyl esters of acrylic and methacrylic acids in presence of benzoyl peroxide showed that, with the exception of 2-naphthyl vinyl ether, the vinyl ethers readily copolymerized with formation of colorless products varying in composition according to the initial monomer ratio. Copolymerization with acrylic esters in presence of benzoyl peroxide (0.2%) was carried out in sealed tubes at 60° for 68 hours. Six pairs of monomers, taken in various molecular proportions, were investigated. The characteristics of the copolymers are given in Table 2.

SUMMARY

1. As a result of the study of the polymerization and copolymerization of cyclohexyl vinyl, decahydro-2-naphthyl vinyl, and 2-naphthyl vinyl ethers by the ionic and free-radical mechanisms, the conditions were found for the preparation in good yield of their polymers and their copolymers with ethyl vinyl, butyl vinyl, and phenyl vinyl ethers, which were obtained in presence of boron trifluoride.

2. The conditions were found for the preparation of polymers in presence of benzoyl peroxide and of 2,2'-azobis[2-methylpropionitrile], and also for the preparation of copolymers of the vinyl ethers with methyl esters of acrylic and methacrylic acids in presence of benzoyl peroxide.

3. The vinyl ether contents of the copolymers depend on the initial monomer ratios.

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TRANSFORMATIONS OF CELLULOSE AT ELEVATED TEMPERATURES

COMMUNICATION 3. FORMATION OF LEVOGLUCOSAN FROM β-D-GLUCOSE

O. P. Golova, E. A. Andrievskaya, A.M. Pakhomov, and N. M. Merlis

The question of the formation of levoglucosan from β-glucose is of considerable interest because several investigators have expressed the view that the vacuum thermodegradation of cellulose to levoglucosan passes through the intermediate formation of glucose [1]. However, the existing data on the formation of levoglucosan by the action of heat on β-glucose in a vacuum under the conditions for the distillation of the reaction product are not sufficiently conclusive.

Karrer [2] reported briefly on the considerable yield of levoglucosan from β-glucose - not greatly different from the yield obtained from starch. Hann and Hudson [3] obtained a high yield of levoglucosan from glucose, irrespective of its configuration (α or β). However, in neither of these papers is there any information about the identification of the levoglucosan and the amount obtained, and there are no data on the methods by which it was isolated. Picon reported in 1953 that in the thermodegradation of α- and β-glucoses at 250-315° and 10^{-4} mm residual pressure identical distillates were obtained in yields of 66.6 and 66.8%. The author stated that the distillates were mixtures of levorotating glucosans ($[\alpha]_D - 10°$) containing levoglucosan. This author also gave no data on the isolation and identification of levoglucosan [4].

Hence, the identification of levoglucosan in the thermodegradation product from glucose is a problem of fundamental importance. The question of the amount of levoglucosan formed is also of fundamental importance. It is important to establish whether levoglucosan is the main product of the thermodegradation of β-glucose, for only in that case can it be supposed that β-glucose is an intermediary in the formation of levoglucosan from cellulose. In order to resolve these questions we investigated the thermal decomposition of β-glucose under the optimum conditions for the formation of levoglucosan from cellulose.

EXPERIMENTAL *

The β-glucose used was prepared by Behrend's method [5]: crystallization of α-glucose from hot pyridine solution; m.p. 148-150°; initial $[\alpha]_D^{20}$ (eight minutes after dissolution) 22.5°; final $[\alpha]_D^{20}$ 52°. β-Glucose, in the form of tablets, was heated in a vacuum of 10^{-3} mm. The process of thermal decomposition was characterized by the yields of 1) paste-like distillate, which solidified when allowed to stand and which we called technical levoglucosan; 2) readily volatile substances frozen out in a trap by liquid nitrogen; and 3) dry residue. The results are given in Table 1.

It is noteworthy that the paste-like distillate is obtained from β-glucose in a yield of only 42.7%, whereas its yield from cellulose is 76%. It would appear that the remainder of the β-glucose undergoes more profound decomposition with formation of an appreciable amount of volatile substances and gases. The yield of dry residue was 18.2%.

For the isolation of levoglucosan from the paste-like product obtained from β-glucose, we gave a purification treatment with an anion-exchange agent and recrystallized twice from absolute alcohol. We obtained crystalline levoglucosan, m.p. 170-173° and $[\alpha]_D^{20} - 65.1°$; there was no melting point depression in admixture with pure levoglucosan. Further crystallization from alcohol gave levoglucosan of m.p. 173-175°, and this was

*Z. V. Volodina took part in the experimental work.

TABLE 1

Original substance	Yield of decomposition product (%)			
	Paste-like distillate	Readily volatile substances	Gas and losses	Dry residue
β-Glucose*	42.7	34.0	5.1	18.2
Cellulose	76.0	18.0	1.2	4.8
Levoglucosan**	98.8	—	—	—

* For β-glucose the results are means from six experiments.

** Under these conditions levoglucosan distills almost quantitatively.

converted into its benzoyl derivative by the Schotten-Baumann reaction. After three crystallizations from benzene it melted at 199.0°.

Found %: C 68.33; 68.45; H 4.61; 4.68 $C_{27}H_{22}O_8$. Calculated %: C 68.35; H 4.64

There was no melting point depression in admixture with the benzoyl derivative of pure levoglucosan (m.p. 199.5°). The presence of levoglucosan in the product of the thermal decomposition of β-glucose may therefore be regarded as established.

The second of our questions - is levoglucosan the main product of the thermal decomposition of β-glucose? - may be answered by a comparison of corresponding data on the yields of levoglucosan from β-glucose and from cellulose, isolation being carried out under identical conditions (Table 2).

The product obtained from β-glucose and subjected to anion-exchange purification treatment was a cream substance which solidified only partially. Purification of the product of the thermodegradation of cellulose gave a crystalline substance.* The decomposition products were passed in the form of a 20% aqueous solution through 400 ml of the anion-exchange resin in a swollen condition (four successive columns each containing 100 ml of the anion-exchange resin). In the purification of the thermodegradation product from cellulose, the solution was first passed through the anion-exchange resin Anionite AN-1, which ensured very effective decolorization. It was shown beforehand that the losses of levoglucosan in Anionites AN-1 and EDE-10 amounted to about 1.5% per 100 ml of Anionite. These losses were determined by passing solutions of pure levoglucosan through the Anionite (Table 2).

TABLE 2

Thermal-decomposition product	Anionite	Volume of Anionite (ml)	Yield of purified product (% on β-glucose or cellulose)	$[\alpha]_D^{20}$ of purified product	Yield of levoglucosan after recryst. (% on β-glucose or cellulose	M.p. of levoglucosan (°C)
Product from β-glucose	EDE-10	400	28.2	−14.6	5.60	170–173
Product from cellulose	AN-1 EDE-10	200 200	48.1	−52.6	37.5	174–176

As will be seen from Table 2, the yield of levoglucosan from β-glucose was 5.60%; the mother liquor after removal of levoglucosan by crystallization had $[\alpha]_D^{20} = 0$. The yield of levoglucosan from cellulose (purification of the thermodegradation product under the same conditions) was 37.5%. When account is taken of the losses of levoglucosan in the Anionite, the yields of levoglucosan from β-glucose and cellulose are found to be 6% and 39-40% respectively.

* Work on the application of anion-exchange agents for the isolation of levoglucosan from the thermodegradation product of cellulose was carried out in consultation with K. M. Saldadze and will be published separately.

SUMMARY

1. The formation of levoglucosan in the thermal decomposition of glucose was proved by the isolation of levoglucosan with the aid of anion-exchange agents and its identification. The yield did not exceed 6% on the amount of β-glucose taken. Unlike the thermal decomposition of cellulose, in which levoglucosan is the main product, the thermal decomposition of β-glucose yields levoglucosan only as a byproduct.

2. Hydrolysis of cellulose to β-glucose and subsequent dehydration cannot be regarded as the main course taken by the reaction resulting in the formation of levoglucosan in the thermodegradation of cellulose in a vacuum.

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LETTERS TO THE EDITOR

HYDROGENATION CATALYSTS FOR POLYSACCHARIDES

Cellulose is not very reactive, and its hydrolysis with dilute acids requires severe conditions. Under such conditions the monosaccharides formed in the hydrolysis are broken down and are obtained in low yield. Combination of acid hydrolysis with catalytic hydrogenation as a rapid succession of processes makes it possible to convert cellulose and other polysaccharides into the corresponding polyhydric alcohols in almost quantitative yield. If hydrogenation is carried out in presence of more than 1% of sulfuric or phosphoric acid, then these polyhydric alcohols are dehydrated with formation of their monoanhydrides, also in high yield.

We found that a good hydrogenation catalyst for this process is ruthenium, which enabled us to obtain 78-95% yields of the corresponding polyhydric alcohols or their monoanhydrides from cellulose, hemicelluloses, and starch in an acid medium; moreover, there were no free reducing substances in the reaction product. For example, sulfite cellulose, heated in presence of 2% of sulfuric acid and 0.1% of ruthenium supported on charcoal or silica gel at 156-160° for two hours under 70 atm pressure, gave a clear colorless solution, from which the monoanhydride of sorbitol was isolated in 82% yield on the amount of cellulose taken, the amount of combined water being taken into account. Unpurified hemicelluloses (wastes from viscose manufacture), treated with 1% of sulfuric acid in presence of 0.1% of ruthenium at 155-160° and 70 atm for one hour, gave a 78% yield of polyhydric alcohols. Starch reacts still more readily. We found that palladium gives results similar to those obtained with ruthenium.

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Dear Sir:

A detailed experimental investigation of the adsorption isotherms of benzene vapor at 20° and of nitrogen vapor at −195° on active carbons of the first structural type has been carried out by E. G. Zhukovskaya and has shown that the isotherm equation of Dubinin and Radushkevich [1] can be satisfactorily applied in these cases. The difference ΔW_0 between the temperature-independent constants W_0, which express the limiting volumes of the adsorption spaces of nitrogen and benzene, is determined by the ultraporosity effect, i.e., the inaccessibility of part of the volume of the micropores to the larger benzene molecules. This opens up the possibility of studying the distribution of the micropore volume of active carbons with respect to pore size by the method of "molecular probes" [2].

If ΔW_0 is the difference of these volumes for two vapors having different effective molecular radii r_1 and r_2, then the differential micropore volume for the mean radius $\bar{r} = \frac{1}{2}(r_1 + r_2)$ will be expressed by the derivative $\Delta W_0 / \Delta r$, in which $\Delta r = r_2 - r_1$. If we have a selection of substances having molecules of different sizes and as nearly spherical in shape as possible, then it is possible to describe the distribution of most of the micropore volume of the active carbon. Naturally, the higher the molecular weight of the substance, the higher the temperature at which the adsorption isotherms will have to be measured.

M. M. Dubinin

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CURRENT EVENTS

GENERAL MEETING OF THE DIVISION OF CHEMICAL SCIENCES OF THE ACADEMY OF SCIENCES OF THE U S S R DECEMBER 26-27, 1956

A general meeting of the Division of Chemical Sciences of the Academy of Sciences of the USSR was held on December 26-27, 1956 under the chairmanship of Academician M. M. Dubinin. V. I. Spitsyn, Corr. Member of the Academy, read a paper entitled "The Structure of Aquopoly- and Heteropoly-compounds". He pointed out that, in spite of the large number of papers devoted to the investigation of heteropolycompounds, there were still some important questions, related to their structure, conditions of formation, and chemical properties, which remained unresolved. The questions included, for example, the basicity of heteropolyacids, the mechanism and individual stages in the formation of heteropolycompounds, the part played by water in this process, the structure of heteropolyanions as a whole and of the structural units of their inner spheres in particular. The extensively used formulas of Miolati, Rosenheim, and Copaux for the structures of aquopoly- and heteropoly-compounds cannot be regarded as satisfactory. Irrespective of the sizes and chemical nature of the central atoms of heteropolyanions, their coordination numbers are always assumed to be 6. These formulas take no account at all of the part played by water as a structural unit of heteropolyanions. The structural formulas proposed by Pauling, Keggin, and other authors on the basis of crystal chemistry and X-ray investigations probably provide better representations of the structures of heteropolycompounds, but in these also the part played by water as a complex former is not brought out sufficiently clearly. This applies particularly to aquopolycompounds.

The author expressed the opinion that the formation of aquopoly- and heteropoly-compounds depends considerably on the tendency of radicals entering into the complex-formation reaction to be hydrogen-bonded. Hydrogen ions bind together the anions of acids taking part in the formation of the complex ion. It is necessary also to take account of the possible part played by hydroxonium ions in the internal structure of aquopoly- and heteropoly-anions.

A study of the process of self-diffusion in systems containing phosphate and tungstate ions labeled with P^{32} and W^{185} enabled the author to show that interaction between these ions begins already in an alkaline medium and probably proceeds according to the scheme $PO_4H \ldots O_4W$. Systematic investigation of the processes of dehydration of salts of various heteropolyacids led to the conclusion that one or two water molecules are more strongly bound in their anions than others. Experiments on the dialysis of acidified solutions of normal tungstate showed that at pH 7-6 macromolecular anions were formed and then gradually underwent disaggregation. Polymerization of the tungstic acid molecules formed undoubtedly played a part here.

On the basis of these investigations the structure of heteropolycompounds of the phosphomolybdate and silicotungstate types can be expressed by the general formula $H_m[RO_4(H_2XO_4)_{12}(H_2O)_n]$, in which R is a nonmetal complex-former, m is the basicity of the corresponding acid, and X is Mo or W.

Investigation of isotopic exchange in systems containing aquopoly and heteropoly-compounds showed that the hydrogen and oxygen atoms present are very mobile. Exchange of ligands of the inner sphere proceeds stagewise. Exchange of central atoms occurs only in the case of incipient decomposition of the complex anion. In conclusion, the author remarked that the application of the method of labeled atoms to the study of aquopoly- and heteropoly-compounds made it possible to obtain new information about their structure and properties.

Participants in the discussion of the paper included V. A. Kargin, L. V. Tananaev, I. P. Alimarin, Ya. K. Syrkin, A. A. Grinberg, and M. M. Dubinin.

In a paper entitled "Theory of the Direct Analysis of Crystal Structure", A. I. Kitaigorodsky, Doctor of Physicomathematical Sciences, stated that for the study of crystal structure direct methods - which, by the

application of some mathematical procedure, make it possible to derive the structure from the intensity distribution in the X-ray photograph - are of fundamental interest. Several years of work were devoted to the creation of the theory of such a method, free from the requirement that there be preliminary information about the structure and even concerning the chemical composition.

In the work reported the author confined himself to the case of a centrosymmetrical crystal. This is a small limitation, because the great majority of molecules crystallize in centrosymmetrical formations. In this case, in order to calculate the electron density of the crystal from known formulas it is necessary to know the absolute values and algebraic signs of the amplitudes of the diffracted rays that produce the spots on the X-ray photograph. Experiment gives only the absolute value of the amplitude F; the signs of the amplitudes must be determined from other considerations. The author proposed a theory by which the signs of the amplitudes could be determined on the basis of a comparison of the intensities of various interferences. For uncomplicated structures the calculations are simple, but in more complex cases the problem can be solved only by the use of rapid electronic calculating machines, the introduction of which into the practice of structural analysis is a task of the immediate future. The theory shows that direct methods of analysis are possible for structures for which the number of atoms in the unit cell does not exceed 100-200. The presence of a heavy atom among the lighter widens the possibilities of the method. The author declared that the establishment of direct methods of structural analysis would provide a practical solution of an important problem: that of freeing the synthetic chemist from work on the proof of chemical structural formulas.

M. I. Kabachnik, Corr. Member of the Academy of Sciences, read a paper entitled "Investigations on Tautomerism". The author has systematically applied modern theory of acid-base protolytic equilibrium to tautomeric equilibrium and has derived some fundamental quantitative relationships characterizing tautomeric equilibrium. On the basis of the fact that the tautomeric-equilibrium constant is equal to the ratio of the ionization constants of the tautomeric forms in the given medium, he has calculated the ionization constants of the keto and enol forms separately and determined the relationship between acidity and enolizability.

The author proposed a new method for the determination of tautomeric-equilibrium constants from potentiometric-titration data on equilibrium solutions of tautomeric substances. The method was applied to keto-enol and lactim-lactam tautomerism and also to the thione-thiol tautomerism of organophosphorus compounds. An investigation of the dependence of the tautomeric-equilibrium constants of keto-enol compounds on the solvent showed that open-chain keto-enols not containing substituents in the α-position behave like "cis-fixed"enols and therefore form cis enol forms. It was shown experimentally that the enolization of "trans-fixed"enols does not depend on the nature of the solvent. Open-chain keto-enols containing α-substituents which sterically hinder cis enolization contain both cis and trans enol forms in equilibrium.

Since the position of tautomeric equilibrium is determined by the ratio of the ionization constants of the two forms, then, as the author pointed out, in diad-tautomeric organophosphorus systems - dialkyl hydrogen phosphorothioites, dialkyl hydrogen phosphites, and dialkyl N-phenylphosphoramidites - it would be expected that tautomeric equilibrium would be displaced in the direction of the quinquevalent phosphorus tautomer in the first two cases and in the direction of the tervalent-phosphorus form in the third case. Investigation showd the correctness of this supposition. The author investigated also the chemical properties of dialkyl hydrogen phosphorothioites and dialkyl phosphonothioates, which are characterized by the ability to form two series of derivatives in accordance with the presence of thione-thiol tautomerism in these compounds. It was shown that Hammett's equation can be applied to acids of quinquevalent phosphorus. The application of Hammett's equation and the theory of acid-base protolytic equilibrium opens up the possibility of predicting tautomeric-equilibrium constants from a knowledge of the structures of the organophosphorus acids.

Participants in the discussion on this paper included A. I. Brodsky, B. A. Arbuzov, M. M. Dubinin, and M. M. Shemyakin.

O. A. Reutov, Doctor of Chemical Sciences, read a paper entitled "Synthesis of Organometallic Compounds via Diazo Compounds". During the last five years in the course of work directed by the author new methods have been developed for the synthesis of organic compounds of heavy metals via diazo compounds and the mechanisms of the reactions taking place have been studied.

In the development of a method of synthesizing organic compounds of Hg, As, Sb, and Bi via arylazoformates $ArN_2CO_2K + MCl_n \rightarrow ArMCl_{n-1} + N_2 + CO_2 + KCl$ it was found that double diazonium salts formed as byproducts

when reaction is carried out in presence of atmospheric oxygen readily arylate organometallic compounds : $Ar_m MX_{(n-m)} + ArN_2XMX_n \rightarrow Ar_{(m+1)} MX_{(n-m+1)} + N_2 + MX_n$ in which n is the valency of the metal M. This reaction was found to provide a convenient method for the synthesis of organoarsenic and organoantimony compounds of various types.

In general, the methods of synthesizing organoantimony compounds are based on the use of the following double salts : $SbCl_3 \cdot ArN_2Cl$; $ArSbCl_2 \cdot ArN_2Cl$; $SbCl_5 \cdot ArN_2Cl$; $ArSbCl_4 \cdot ArN_2Cl$; $ArSbCl_3 \cdot ArN_2Cl$. The particular organoantimony compound formed was found to be greatly dependent on the conditions under which $SbCl_3 \cdot ArN_2Cl$ was decomposed: the reaction can be directed toward the formation of one or other type of organoantimony compound, and in particular toward the formation of $ArSbX_3$ in high yield.

In a number of cases in which organometallic compounds are obtained in poor yields or are not formed at all, they may be synthesized by the double iodonium salt method proposed by the author. For example, organotin compounds, which are obtained in insignificant yield via diazo compounds by any of the known reactions, are obtained in yields of 50-80% from double iodonium salts. Organic compounds of mercury, antimony, and bismuth can also be prepared via double iodonium salts.

As regards the mechanism of the formation of organometallic compounds via double diazonium salts, it is generally acknowledged (since the investigations of W. Waters) that reactions resulting in the formation of a carbon-metal bond (and particularly the most important of these reactions – the Nesmeyanov reaction) have a free-radical character. However, Reutov has come to the conclusion that Waters' arguments in favor of the free-radical mechanism of these reactions are not sufficiently well grounded.

The hypothesis of the heterolytic character of the decomposition of double diazonium salts with formation of organometallic compounds was confirmed in a study of the stabilities of the double salts $p\text{-}XC_6H_4SbCl_2 \cdot p\text{-}YC_6H_4N_2Cl$.

Apart from investigations on organometallic compounds of the aromatic series, the author reported also his work on the synthesis of organometallic compounds of the aliphatic and aliphatic-aromatic series. A method was developed for the synthesis of organomercury compounds from hydrazones of aldehydes and ketones and mercuric acetate. The reaction proceeds through the stage of oxidation of hydrazones and formation of diazo compounds. Various types of organomercury compounds can be formed, depending on the structure of the original hydrazone and the reaction conditions.

Participants in the discussion on this paper included V. V. Voevodsky, P. G. Sergeev, A. N. Nesmeyanov, and B. A. Dolgoplosk.

When the reading of papers was complete, the President of the D. I. Mendeleev All-Union Chemical Society, I. P. Losev, Doctor of Chemical Sciences, gave an address on the organization of the Eighth Mendeleev Congress in 1958. After an exchange of views, in which I. L. Knunyants, N. M. Zhavoronkov, N. N. Semenov, A. P. Vinogradov, A. L Brodsky, A. N. Frumkin, M. M. Dubinin, S. L Volfkovich, and S. N. Danilov took part, the question of the desirability of calling the Congress was put to the vote and approved. The Chairman, Academician M. M. Dubinin, recommended that, in future discussions on the calling of the Congress, the President of the Mendeleev All-Union Chemical Society should take account of the views expressed at the General Meeting of the Division of Chemical Sciences and of the wishes of members of the Division.

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Division of Chemical Sciences

IN ENGLISH TRANSLATION

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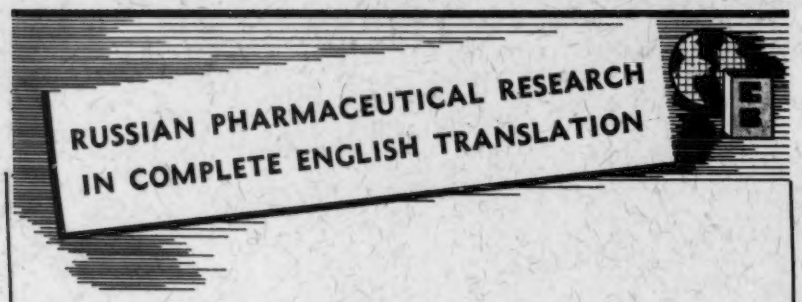

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